**Method 202 Assessment and Evaluation for Bias and Other Uses**
**Evaluation of Stakeholder Recommendations**
**August 4, 2006 through April 17, 2007**
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| 9/5/06 (4, 5) | Roger Shigehara, Walt Smith, Emission Monitoring, Inc. | Would operating at above ice-bath reduce the amount of $SO_2$ to a "tolerable" level at >10% moisture? Another concern would be the effect of temperature on the organic fraction. | Experimental data show that increasing the temperature of the condenser, water drop out, first impinger, and cool filter to 85°F (30°C) reduces the conversion and capture of $SO_2$. |
| 9/6/06 (6) | Naomi Goodman, EPRI | Maintaining the condenser and impinger before the cold filter at 68°F sounds logical, but may be awkward to apply in practice. You would need separate cooling systems for the first impinger and for the impingers after the filter. This goes against your goal to use standard glassware and equipment. Clarify whether the condenser temperature will change with this addition. The test plan doesn't specify a condenser temperature, but the Richards, et al. paper on which you based the dry impinger method cites "below 68°F." How much volume would you expect the impingers after the filter to collect at low (5%) and high (15%) moisture conditions? Depending on the volume of water, you could still get a significant artifact from $SO_2$ dissolved in the second and third impingers. | The approach for elevating the condensable particulate capture temperature to 85°F was demonstrated in laboratory experiments. Stakeholder and equipment vendors indicated the changes in sampling train needed to implement the elevated temperature were similar to other methods EPA currently requires. The distribution of water collected from a source simulation of 10% moisture was provided during a stakeholder meeting and are available elsewhere. Approximately 50% of the water is collected after the filter when the source simulation was performed at 10% moisture. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 9/11/06 (7) | Clifford Glowacki, Measurement Technologies | The higher temperature suggested by EPRI and Emission Monitoring is a good modification. | Based on Stakeholder comments and laboratory confirmation, EPA will pursue a method that limits the temperature in the Method 202 sampling train to 85°F (30°C) prior to the final (ambient) temperature filter. |
| 9/5/06 (4, 5) | Roger Shigehara, Walt Smith, Emission Monitoring, Inc. | We highly recommend the use of HCl. We recommend the following experiments: 1) Determine whether 0.01N HCl (or some other concentration) would effectively minimize the $SO_2$ absorption and, hence, the amount of CPM from $SO_2$ artifact. 2) If purging is marginally acceptable, then conduct the following experiment (see e-mail for details), 3) To determine the effect of $NH_3$, conduct the following experiment. (see e-mail for details). | Stakeholder Environment Canada will pursue limited HCl laboratory studies. EPA does not plan to investigate addition of HCl due to the potential for artifact formation when ammonia is present in the stack emissions. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 9/6/06 (6) | Naomi Goodman, EPRI | The addition of sulfuric acid does not make sense. As you note, the inaccuracy in the weight of added acid could overwhelm the actual CPM measurement. Adding HCl is worth attempting, but as you point out, will work only for sources that do not have free ammonia. Note that ammonia solubility increases at low pH, so the potential for ammonium chloride artifact formation would be greater for a given concentration of gaseous ammonia.<br><br>One concern with this approach is what the pH adjustment would do to organic condensables. Phenols can react with $NO_x$ at very low pH to form nitrophenols. If there are further aqueous condensation reactions, you could be creating artifactual organic CPM. | Good clarification and addition to the potential artifacts that may be caused by adding HCl to the Method 202 impingers. We are in general agreement with the concern about generating additional artifacts since the dry impinger modification plus nitrogen purging the sampling train have reduced the artifact by more than 90%. To achieve lower artifact, Conditional Test Method 0039 (dilution sampling) is an alternative. |
| 9/11/06 (7) | Clifford Glowacki, Measurement Technologies | The addition of HCl is a good modification. | See response to 9/5/06 Shigehara |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 9/5/06 (4, 5) | Roger Shigehara, Walt Smith, Emission Monitoring, Inc. | Regarding stabilization of sulfite to avoid artifact formation from $SO_2$, we recommend that this be investigated for the benefit of the overall CPM lab experiment. The investigation should not be difficult to do. Bubble $SO_2$ gas directly from cylinder into water and add glycerin. If the sulfite concentration remains stable, the procedure works.<br><br>The subtraction procedure will be difficult to apply. The subtraction assumes that the sulfite content remains constant, i.e., is lost during the evaporation process. Adding an oxidizer to convert the sulfite to sulfate so that the proper amount of sulfite can be subtracted may complicate matters with other CPM. | Laboratory experiments to stabilize $SO_3$ were performed on samples after collection. Glycerin stabilizes sulfite. However, glycerin does not evaporate from samples and would be counted as a CPM. The commenter is correct that the correction factor would be difficult to apply. Therefore, addition of glycerin is not included in the revised method. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 9/6/06 (6) | Naomi Goodman, EPRI | The purpose of stabilizing the (sulfite/sulfate) ratio is not clear. EPRI research also indicates that the pre-evaporation impinger liquid can contain sulfites, but that the sulfite is completely converted to sulfate during evaporation of the impinger residue. Since the evaporation step is part of Method 202, and is also part of the dry impinger technique, it is irrelevant which species is present in the impinger. The distinction is only important if ion chromatography of the non-evaporated impinger water is used to quantify CPM, rather than a gravimetric technique. In addition, subtraction of sulfite from CPM is probably not appropriate, since sulfite will react quickly with moisture or $NO_x$ in the atmosphere to form sulfuric acid.<br><br>If you want to determine the ratio for research purposes, in order to better understand the chemistry occurring in the impingers, the approach you have suggested is reasonable. | Ion chromatography is not currently included in the modified Method 202 procedure to quantify CPM. No further investigation to stabilize sulfite is planned. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
|---|---|---|---|
| 9/5/06 (2, 3) | Emil Stewart, Mactec | Regarding the filter after the third impinger, do you weigh it or do you include it with the water and extract with $MeCl_2$ later? If you weigh it, is it organic or inorganic? | We're following the method that John Richards developed as the starting point. We've assumed the final method will say that the "cold" (a.k.a. ambient) temperature filter will be pre-weighed. After sampling the filter will be recovered as a weigh-able filter, desiccated to constant weight at ambient similar to the weighing for Method 5 filterable particulate. It doesn't matter if the filter catch is organic or inorganic, it is currently considered CPM.<br><br>We're also determining the maximum temperature allowable at the exit of the cold filter. Assume for now that the temperature must be "summer" ambient and that the method will require monitoring and reporting of the cold filter exit temperature. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 3/14/07 (20-23) | Michael Klein, New Jersey Department of Environmental Protection - Bureau of Technical Services | The current Method 202 implies, but does not explicitly detail, the procedures for volume correcting the blanks. | The volume specified for the reagent blanks is nominally the same as we expect sampling firms to use in the field. As written Method 202 specifies the amount of water to be added into the cold impingers and the blank results should be corrected for the actual volume used.<br><br>If the blank values are low, which they should be if the sampling firm used quality reagents and didn't contaminate them in the field, then the impact of not correcting for the volume used is small. If the blank in 100 mL is large and the sampling firm used 300 mL or more, then the correction could be off by a factor of three. However, not correcting for the additional blank solvent volume could bias the results high and penalize the regulated source.<br><br>Alternatively, if the organic blank is high and the volume used for the organic rinse is small, then the volume correction could reduce the blank contribution. Not correcting the train results for smaller volume of organic reagent (smaller than used to determine the blank) could bias the results low and reward the regulated source.<br><br>The final method will allow correction for blank/reagent mass up to a specified limit. |

**Method 202 Assessment and Evaluation for Bias and Other Uses**
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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
|---|---|---|---|
| 8/4/06 (1) | Naomi Goodman, EPRI | EPRI's proposal was to add several additional flue gas mixtures and to test two methods to correct for, rather than reduce, the sulfuric acid bias. However, feedback in the August 1, 2006 stakeholder meeting was that EPA prefers to evaluate methods that have the potential to address all bias mechanisms. Hopefully, the results that ERG will report will at least partially answer this question. Or it may be that more testing will be required. | EPA reported experimental results that showed the dry impinger modification to Method 202 reduced sulfur dioxide artifact formation by more than 90%. EPRI submitted a proposed test plan to supplement ERG's QAPP/Test plan. The proposed test plan included several tasks including: comparison of Method 202 with the proposed dry impinger modification to Method 202 at higher simulated water and higher sulfur dioxide concentrations; addition of sulfuric acid to the stack simulation gas and comparison of Method 202 with the controlled condensation sampling method and a lower temperature prefilter condensable sampling train. The EPRI test plan will add to the understanding of sulfur dioxide artifact formation at higher moisture and higher sulfur dioxide concentrations. It will also be the first test of the dry impinger method challenged with a known quantity of condensable material. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 4/3/07 (25-27) | William R. Prokopy, DaimlerChrysler Corporation | Is it the intent of the draft method to mix the blanks? Regarding the sample and blank correction, the addition of acetone to clean out the impingers before the methylene chloride rinse is an additional variable to take into consideration and the method should be clear that all blank reagents, water, acetone and methylene chloride must be normalized to mass. It appears this is addressed by the use of exactly 100 mL of each blank, but perhaps the method should state clearly the volume to eliminate any confusion or mishandling of the blanks with respect to blank subtraction.<br><br>Regarding what is happening to the acetone in the separatory funnel, are we interested in where the acetone goes, be it the water, or methylene chloride? If no, and all that really matters is the final mass, then why do we separate the inorganics from the organics for this type of application? Why not simply dry down and record? | EPA rewrote revisions to Method 202 sections 11.2.10, 11.2.11, and 11.2.12, which contain the procedure for determining the residual weight of the reagent solvents used to recover samples from the combined Method 201/202. These three sections now contain the information to process reagent blanks and eliminate cross references to other procedures in the method.<br><br>EPA made two fundamental changes: First, a known quantity of reagent blank (water, acetone, and methylene chloride) should be evaporated to dryness without regard to organic or inorganic residual contents. That means the water does not need to be extracted with methylene chloride to divide the blank between organic and inorganic material. Second, as with EPA Method 315 (developed to determine organic extractable material for aluminum smelters), we've changed the procedure to require drying the sample in a dessicator for 24 hours followed by a single weighing to 0.1 Mg rather than a requirement to weight to a constant weight. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 4/11/07 (29-30) | David Moll, ENSR/AECOM | 1) What is the total number of impingers in the sampling train? | There are a total of four impingers in the sampling train. The first two impingers are not maintained in the ice bath but are maintained at or below 85°F. The trains that we have assembled and the ones used by one other stakeholder use two sampling boxes but the equipment vendors have said that a large box could be used with a divider to separate the first two and last two impingers. |
| 4/11/07 (29-30) | David Moll, ENSR/AECOM | 2) Are two separate water/ice baths required and what should the condenser coil and knockout impinger temperature range be operated at? And what temperature range should the rest of the impingers and cold filter should be? Is the cold filter tarred and reweighed after sampling? I read 85°F or less. Does this mean I can make it as low as I want, below 68°F, which is typical for most sampling trains? | The first two impingers should not be in an ice bath. The rationale is that the solubility of $SO_2$ in water is greater at the lower temperature and we want to limit the solubility of $SO_2$ in the water. As a result you should run the first two impingers at as high of a temperature that you feel is reasonable not to exceed 85°F at the exit of the filter following the first two impingers. |
| 4/11/07 (29-30) | David Moll, ENSR/AECOM | 3) Please confirm that the purge includes the first impinger after replacing the stem to reach the knockout condensate and the condensate is part of the sample which is why it needs to be purged. One diagram we saw showed the purge location after the 1st impinger. | We purge both of the first two impingers. Yes, all the condensate collected in the condenser and the first two impingers are part of the sample. It may be necessary to add as much as 50 mL degassed reagent grade water to the first impinger to ensure nitrogen completely purges $SO_2$ from the condensate. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 4/11/07 (29-30) | David Moll, ENSR/AECOM | 4) Is HPLC water used for the dry impinger Method 202 water rinses? | The highest quality reagent water should be used to recover samples from the dry impinger modification to Method 202. ASTM Type II water or better will be specified in the method. HPLC water typically meets these requirements and should be evaluated for residual mass. In our experimental evaluation of the revised method two stakeholders and EPA have encountered problems with solids in their reagents (water, acetone and methylene chloride). It would be wise to verify that the solids contents of any reagents that you use are absolutely insignificant. You could use manufactured laboratory water (doubly distilled and filtered) but you need to verify the quality of the water you produce. |
| 2/7/07 (14) | Roger Shigehara, Emissions Monitoring | No experiments have been done with ammonia and its effect on artifacts. Suggestion: Use a separate method for $SO_3$, using the controlled condensation method or modified Method 8 (method with a prefilter for PM solids) or analyzing for sulfates (assuming that $SO_3$ is the only significant inorganic condensable). The latter would meet the goal of using one sampling train for both organics and inorganics. Use HCl with reduced reagent volume in impingers. | We will perform a limited set of experiments to evaluate the effects of ammonia on the dry impinger modification to Method 202. We will not pursue a separate method to correct for sulfite and/or $SO_2$ artifacts beyond the dry impinger modification evaluation currently underway. Stakeholders may contribute additional data from methods used to correct sulfite and sulfate capture in the revised Method 202. It is inappropriate to assume that $SO_3$ is the only significant inorganic condensable for all sources. See previous response to Shigehara 9/5/06 on the HCl recommendation. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 8/4/06 (1) | Naomi Goodman, EPRI | EPRI's proposal was to add several additional flue gas mixtures and to test two methods to correct for, rather than reduce, the sulfuric acid bias. However, feedback in the August 1, 2006 stakeholder meeting was that EPA prefers to evaluate methods that have the potential to address all bias mechanisms. Hopefully, the results that ERG will report will at least partially answer this question. Or it may be that more testing will be required. | EPA reported experimental results that showed the dry impinger modification to Method 202 reduced sulfur dioxide artifact formation by more than 90%. EPRI submitted a proposed test plan to supplement ERG's QAPP/Test plan. The proposed test plan included several tasks including: comparison of Method 202 with the proposed dry impinger modification to Method 202 at higher simulated water and higher sulfur dioxide concentrations; addition of sulfuric acid to the stack simulation gas and comparison of Method 202 with the controlled condensation sampling method and a lower temperature pre-filter condensable sampling train. The EPRI test plan will add to the understanding of sulfur dioxide artifact formation at higher moisture and higher sulfur dioxide concentrations. It will also be the first test of the dry impinger method challenged with a known quantity of condensable material. |
| 3/29/07 (24) | Krishna Row, Pine Bend Refinery Flint Hills Resources | Conduct engineering analysis of the modified Method 202 on a process heater. | We do not plan to evaluate the modified Method 202 on all source categories. Stakeholders are encouraged to test the methods on sources of particular interest to them or their industry sector. |
| Topic: Test dry impinger at higher moisture and $SO_2$ levels | | | |

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| 9/11/06 (8) | George Marson, Environment Canada | Test the EC train at higher moisture and higher $SO_2$ level.<br>EC observed the following:<br>• The inorganic CPM artifact caused by $SO_2$ may be reduced to approximately 2 mg or less by EC's dry impinger version of Method 202.<br>• A ten fold increase in $SO_2$ level caused only a modest increase in inorganic CPM artifact.<br>• Nitrogen gas volume is similar to the sample volume, and should be filtered to the same extent.<br>• The drying and weighing of condensate on the same glass jars requires special consideration to the effects of changes in atmospheric pressure and weighing room temperature<br>• The quantitative transfer of redissolved condensate to weighing pans should be described in the method.<br>• Nitrogen purge at ambient temperature is likely to be more effective than the prescribed purge at ice bath temperature. | EPA agrees with EC's observations and duplicated EC's procedures in EPA's final experiments that were used to determine precision and bias of EPA's modified Method 202 train.<br><br>EPA found that evaporating samples to near dryness in glass beakers followed by transfer to aluminum pans and evaporation to dryness successfully avoided issues with weighing wide mouth heavy glass containers.<br>EPA will also recommend desiccation of samples for 24 hours following Method 315 which will avoid much of the variation caused by changes in temperature and atmospheric pressure for weighings currently done on successive days. |

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| 9/18/06 (9) | George Marson, Environment Canada | How does zero headspace or the removal of oxygen from samples with oxygen scavengers affect CPM? EC observed the following: 1) the ammonia neutralization of condensate should be carried out immediately after sample degassing or on a little volume of redissolved evaporation residue, otherwise the rising pH will ensure the reaction of any dissolved $O_2$ in the liquid (which then becomes 6 times as much CPM artifact). 2) Given the reactivity of sulfite, Method 202 is in big trouble if a source has less $SO_2$ than ammonia slip, so that the condensate is neutral or alkaline. | EPA believes that the nitrogen purge of samples immediately after sampling is adequate to remove $SO_2$, thus eliminating the concern for artifacts due to air oxidation. |

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| Date and Index # | Stakeholder | Comment/Question/ Recommendation | EPA Response/Conclusion |
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| 1/7/07 (10) | George Marson, Environment Canada | Theoretically determine which CPM is retained in samples after evaporation at ambient temperature. EC confirmed that CTM-039 and Method 202 should theoretically produce similar organic CPM results, except for samples containing mid-range vapor pressure compounds (approximately 0.001 – 0.01 mm Hg @ 20°C) for which the Method 202 results would be higher than CTM-039. The discrepancy between the two methods depends on the hydrocarbon level of the samples, and the temperatures of the CTM-039 filter, and the Method 202 condenser. | EPA has historical empirical data that agree with EC's conclusion. |
| 2/1/07 (12) | George Marson, Environment Canada | Determine the effect of evaporation time on retention of CPM. EC concluded that water must be evaporated to a small volume (10-20 ml) at an elevated temperature, then evaporated to dryness at ambient temperature. Final evaporation to dryness should be done in 24 hours or less. | EPA agrees that the final evaporation at ambient temperature should be done in 24 hours or less. Laboratory experience confirms EC's conclusion that 10 mL of aqueous condensate evaporates to dryness at room temperature in less than 24 hours when the evaporation is performed in an aluminum weighing pan. |
| 2/2/07 (13) | Steve Eckard, Enthalpy | Enthalpy has evaluated $H_2SO_4$ losses using the modified procedure at three different temperatures. | No results received to date. |
| 2/16/07 (15-19) | George Marson, Environment Canada | Determine if the $H_2SO_4$ can be measured as CPM without displacing waters of hydration. | EC performed a series of experiments with organic material and sulfuric acid mixes and concluded that this cannot be done. |

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| 2/20/07 (16) | George Marson, Environment Canada | Find a better dessicant that will allow evaporation of $H_2SO_4$ without removing the waters of hydration. | EC and EPA investigated dessicants and concluded that the best common dessicant found is anhydrous calcium sulfate. However, the best common dessicant cannot dry $H_2SO_4$ without addition of ammonia to remove the waters of hydration. |
| 2/28/07 (19) | George Marson, Environment Canada | Evaluate the retention of selected organic and inorganic materials in the modified Method 202 analytical procedures. | EC's conclusions supported the theory that compounds with vapor pressure below the $C_{17}$ hydrocarbon would be retained. |
| 4/17/07 (31) | George Marson, Environment Canada | Determine if organic and inorganic material can be evaporated to dryness without separating the organic and inorganic fractions. | EC concluded that drying jointly the $MeCl_2$ rinses and condensate together is an utter failure. |

**From:** "Goodman, Naomi" <Ngoodman@epri.com> ***Index 1***
**To:** <Myers.Ron@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>
**Date:** Fri, Aug 4, 2006 3:39 PM
**Subject:** RE: Comments on Test Plan and Funding of Supplemental Method 202 Studies

Ron;

I have no further comments on the Test Plan, but want to reiterate EPRI's support for this effort. I held a webcast for utilities interested in the topic and had a strong positive response. This is an important topic for the electric power industry, and EPRI is committed to collaborating with EPA on this topic.

Based on our discussions at the Stakeholder meeting, the scope of work that EPRI will fund needs further discussion. My proposal to ERG was to add several additional flue gas mixtures and to test two methods to correct for, rather than reduce, the sulfuric acid bias. However, your feedback in the meeting was that EPA prefers to evaluate methods that have the potential to address all bias mechanisms. I understand this viewpoint; it would certainly be preferrable to have one method that all sectors can use. However, the preliminary results reported at the meeting cast some doubt on whether the dry impinger method would produce a sufficient reduction in sulfuric acid bias to be helpful. Hopefully, the results that Ray will report next week will at least partially answer this question. Or it may be that more testing will be required before EPA can make an informed decision.

To complete arrangements with EPRI's funders, I will need to determine a scope of work and approximate level of funding needed for EPRI's contribution. At the moment, the funding paperwork is on hold until I can provide this information to the funders. I'm open to discussing various roles for EPRI's involvement, including conducting pilot plant tests after the initial laboratory work is completed.

Please contact me at your convenience. I'm on travel M-Th next week, but will be checking voice/email.

Naomi Goodman

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From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Wednesday, July 26, 2006 11:38 AM
To: Goodman, Naomi; Logan.Thomas@epamail.epa.gov
Cc: Ray.Merrill@erg.com; Nott, Babu; Mcalister.Gary@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Oldham.Conniesue@epamail.epa.gov; Segall.Robin@epamail.epa.gov
Subject: Re: Comments on Test Plan and Funding of Supplemental Method 202 Studies

Naomi:

If it is OK with you and your members, I would like to incorporate your desired additional studies within the laboratory study and QA plan that we are preparing. While EPA may not perform all of the work contained

in the consolodated plan, I see great advantages in a unified plan. This way everyone will know what everyone would like to have and then each stakeholder can select the components of the plan that concerns them most. If you have not already provided Ray with the specifics of the gas matrix for the other coals which interest you and your members, please do so as expediciously as you can. If you can not get him the compositions by tomorrow, I will have him put a placeholder matrix using his best guess at what you would like. I will also have him put two placeholders in the plan for the two additional methods.

My intention in to post material to EPA's web site as "draft" material soon after the paying organization is satisfied that it will not change from further scrutiny by them. As a result, data Ray generates will be reviewed by a few internal EPA technical types (Gary McAlister, Tom Logan, Peter Westlin, Robin Segall) revised to address our comments and then posted to a place where everyone has access to the data.

I would like to complete this laboratory study project by the end of the calendar year. But I would also like to incorporate as many stakeholders work as well. At this time I havn't formed an opinion on how long I will wait for external data. If you could give me an idea of what time you may require, that may help me form an opinion.

Drafting a revised test method will definitely take longer that making the data available.

EPRI Comments on EPA Work Plan.pdf

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-----"Goodman, Naomi" <Ngoodman@epri.com> wrote: -----

To: Ron Myers/RTP/USEPA/US@EPA
From: "Goodman, Naomi" <Ngoodman@epri.com>
Date: 07/26/2006 01:17PM
cc: Ray.Merrill@erg.com, Babu Nott <BNOTT@epri.com>
Subject: Comments on Test Plan and Funding of Supplemental Method 202 Studies

Ron;

Attached are EPRI's comments on the July 14, 2006 draft of the

Test Plan, for your use and for distribution to other stakeholders.

EPRI is interested in funding additional studies to supplement the EPA's scope of work. The tasks that we are interested in funding are as follows:

1. Addition of one or more "coal" flue gas mixtures to the Plan, to better reflect the range of contaminant concentrations.

2. Testing two alternative methods to eliminate the bias of Method 202. The methods of greatest interest are use of the EPRI low-temperature filter and the controlled condensate system (CCS) to correct for the sulfate bias in the Method 202 impingers.

EPRI's funding would also cover preparation of a supplemental work plan by either ERG or an EPRI contractor, and reporting of EPRI-funded data by ERG.

I have discussed these additions with Ray Merrill and have received "ballpark" cost estimates for the above scope of work. The final scope of work that EPRI funds will depend on the interests of the other stakeholders as well as our available funding.

The accelerated schedule for this project is of concern, as EPRI currently does not have the funding in house. I do have verbal commitments from a number of utilities, and strong interest from others, but it will take more than a month to process agreements and contract with ERG. I would like to discuss how EPRI and other stakeholders can support the work and still work within your schedule.

In order to confirm EPRI member funding of these studies, I will need to provide the funders with a schedule of completion for the project, including publication of the Conditional Test Method. I also need to let funders know whether they will have access to EPA's data in 2006, or if they will need to wait until the data are published as a CTM.

I'm looking forward to discussing this with you at the August 1 meeting.

Naomi Goodman

<<EPRI Comments on EPA Work Plan.pdf>>

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***Index 2***

**From:** "Stewart, Emil" <EWSTEWART@mactec.com>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Tue, Sep 5, 2006 7:33 AM
**Subject:** mod 202 dry imp train optional (?) filter

Hi Ray,

This is a followup to mike maret's question regarding the filter after the third impinger - do you weigh it or do you include it with the water and extract with MeCl2 later? If you weigh it, is it organic or inorganic? Assume inorganic since most organics soluble in water? (is that true?) (its early yet!)

Is the filter really optional? What determines when you should use one?

-e

Emil Stewart

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**CC:** "Werner, Arthur" <ASWerner@mactec.com>, "Maret, Michael" <MDMARET@mactec.com>

***Index 3***

**From:** "Stewart, Emil" <EWSTEWART@mactec.com>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Tue, Sep 5, 2006 9:23 AM
**Subject:** RE: mod 202 dry imp train optional (?) filter

Thanks Ray, that makes sense.

-e

-----Original Message-----
From: Ray Merrill [mailto:Ray.Merrill@erg.com]
Sent: Tuesday, September 05, 2006 9:05 AM
To: Stewart, Emil
Cc: myers.ron@epa.gov; Ray Merrill
Subject: Re: mod 202 dry imp train optional (?) filter

Emil
We're following the method that John Richards developed as the starting point.
We've assumed the final method will say that the "cold" (a.k.a. ambient) temperature filter will be preweighed. After sampling the filter will be recovered as a weigh-able filter, dedicated to constant weight at ambient temperature in a desiccator similar to the weighing for method 5 filterable particulate. It doesn't matter if the filter catch is organic or inorganic, it is currently considered condensable particulate material.

We're also determining the maximum temperature allowable at the exit of the cold filter. Assume for now that the temperature must be "summer" ambient and that the method will require monitoring and reporting of the cold filter exit temperature.

I've copied Ron on this note, he may have additional guidance.

Ray

>>> "Stewart, Emil" <EWSTEWART@mactec.com> 9/5/2006 7:30:03 AM >>>
Hi Ray,

This is a followup to mike maret's question regarding the filter after
the third impinger - do you weigh it or do you include it with the water
and extract with MeCl2 later? If you weigh it, is it organic or inorganic? Assume inorganic since most organics soluble in water? (is that true?) (its early yet!)

Is the filter really optional? What determines when you should use one?

-e

Emil Stewart

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P.O. Box 12077

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5001 South Miami Boulevard
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<mailto:FirstInitialMiddleInitialLastName@mactec.com> Web
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***Index 4***

**From:** "Roger Shigehara" <rshigehara@mindspring.com>
**To:** <Myers.Ron@epamail.epa.gov>, <PMUELLER@epri.com>, <Huntley.Roy@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Nizich.Sharon@epamail.epa.gov>, <Parker.Barrett@epamail.epa.gov>, <Westlin.Peter@epamail.epa.gov>, <Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov>, <Oldham.Conniesue@epamail.epa.gov>, <marksh@kochind.com>, <Sorrell.Candace@epamail.epa.gov>, <glenn.england@ge.com>, "'Garry Brooks'" <garry.brooks@erg.com>, "'John Richards'" <john.richards@aircontroltechniques.com>, <shannon.vogel@ncmail.net>, <Driscoll.Tom@epamail.epa.gov>, <ngoodman@epri.com>, "'Dominic Cianciarelli'" <Dominic.Cianciarelli@ec.gc.ca>, <hschiff@trcsolutions.com>, "'Joe Fanjoy'" <joe.fanjoy@erg.com>, <Hardin.Erik@epamail.epa.gov>, <seebea@dnr.state.wi.us>, <mstewartdouglas@4cleanair.org>, "'Karl Loos'" <karl.loos@shell.com>, "'Roy Owens'" <roy.owens@owenscorning.com>, <frank.jarke@ps.ge.com>, <cglowacki@technikonllc.com>, <DCLINE@dem.state.in.us>, <Segall.Robin@epamail.epa.gov>, "'Bill Walker'" <bwalker@cleanair.com>, "'Walt Smith'" <walt@waltersmith.com>, <LSRitts@HHLAW.com>, <JSchultz@steel.org>, "'Christopher Van Atten'" <vanatten@mjbradley.com>, "'Randy Bower'" <randy.bower@erg.com>, "'Michael Palazzolo'" <michael.palazzolo@alcoa.com>, "'Jerry Fulmer'" <jbfulmer@aol.com>, "'Jeffrey Lettrich'" <jeffrey.lettrich@alcoa.com>, "'Patricia Strabbing'" <pas2@daimlerchrysler.com>, "'Mary Snow-Cooper'" <ms14@daimlerchrysler.com>, "'Kathleen Hennessey'" <kmh17@daimlerchrysler.com>, "'Debby Rowe'" <das24@daimlerchrysler.com>, "'Marc Deslauriers'" <Marc.Deslauriers@ec.gc.ca>, <Shine.Brenda@epamail.epa.gov>, "'Bruce Steiner'" <BruceS@steel.org>, "'Steve McDaniel'" <asmcdaniel@aqm.co.knox.tn.us>, "'Mark Lutrzkowski'" <Mark.Lutrzykowski@state.de.us>, "'Jeff Hege'" <jhege@indygov.org>, <linak.bill@epamail.epa.gov>, "'Danny Greene'" <Danny.Greene@erg.com>, "'Joseph Martini'" <joseph.martini@state.de.us>, "'Jeffrey Rogers'" <jeffrey.rogers@state.de.us>, <Gary.Helm@Conectiv.com>, <wreistad@tristategt.org>, <ValmontH@kochind.com>, <George.Marson@ec.gc.ca>, "'Cory Wind'" <wind.cory@deq.state.or.us>, "'Ralph Roberson'" <roberson@rmb-consulting.com>, <Foley.Patrick@epamail.epa.gov>, <Krishna.Row@fhr.com>, <wrp6@daimlerchrysler.com>, <Ray.Merrill@erg.com>, <BOConnor@paprican.ca>, <lfreeman@hunton.com>, <l_carlson@src-ncasi.org>, "'Ashok Jain'" <AJain@src-ncasi.org>
**Date:** Tue, Sep 5, 2006 9:57 PM
**Subject:** RE: Method 202 Improvement Workshop notes.

Ron,
Attached Walt's and my comments.
Roger

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Friday, August 18, 2006 3:23 PM
To: PMUELLER@epri.com; Huntley.Roy@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Nizich.Sharon@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Westlin.Peter@epamail.epa.gov; Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov; Oldham.Conniesue@epamail.epa.gov; marksh@kochind.com; Sorrell.Candace@epamail.epa.gov; glenn.england@ge.com; Garry Brooks; John Richards; shannon.vogel@ncmail.net; Driscoll.Tom@epamail.epa.gov; ngoodman@epri.com; Dominic Cianciarelli; hschiff@trcsolutions.com; Joe Fanjoy; Hardin.Erik@epamail.epa.gov; seebea@dnr.state.wi.us; mstewartdouglas@4cleanair.org; Karl Loos; Roy Owens; frank.jarke@ps.ge.com; cglowacki@technikonllc.com; DCLINE@dem.state.in.us; Segall.Robin@epamail.epa.gov; Bill Walker; Walt Smith; LSRitts@HHLAW.com; JSchultz@steel.org; Christopher Van Atten; Randy Bower; Michael Palazzolo; Jerry Fulmer; Jeffrey Lettrich; Patricia Strabbing; Mary Snow-Cooper; Kathleen Hennessey; Debby Rowe; Marc Deslauriers; Shine.Brenda@epamail.epa.gov; Bruce Steiner; Steve McDaniel; Mark Lutrzkowski; Jeff Hege; linak.bill@epamail.epa.gov; Danny Greene; Joseph

Martini; Jeffrey Rogers; Gary.Helm@Conectiv.com; wreistad@tristategt.org; ValmontH@kochind.com; George.Marson@ec.gc.ca; Cory Wind; rshigehara@mindspring.com; Ralph Roberson; Foley.Patrick@epamail.epa.gov; Krishna.Row@fhr.com; wrp6@daimlerchrysler.com; Ray.Merrill@erg.com; BOConnor@paprican.ca; lfreeman@hunton.com; l_carlson@src-ncasi.org; Ashok Jain
Subject: Method 202 Improvement Workshop notes.

Method 202 improvement project stakeholders:

While I said that I would post the notes on the August 1 workshop on the EMC website within a week, I have encountered more difficulties that I had expected. These notes were posted earlier this week, but I have not had time to send you notification or their location until now. The location is at the bottom of the Method 202 Frequently Asked Questions (FAQ) page ( http://www.epa.gov/ttn/emc/methods/method202.html ). You can get to the bottom of the page a little quicker if you select the question What is EPA doing to assess and reduce artifact formation in Method 202? While we usually send meeting notes to attendees for correction before distributing the notes more widely, I felt this was more expeditious and wanted everyone to get the information as quickly as possible and to encourage other potential stakeholders to participate. I would as you to review the notes and let me know if there is anything that should be revised. For example if we misquoted one of your statements or we missed a point that you felt was important.

In addition, Ray and I indicated that we would provide you with an update of our analyses of the twelve samples that we performed to evaluate the difference between Method 202 and the dry impinger modification proposed by John Richards. The impinger samples have still not been weighed to a constant mass but I expect that by early next week, I should be able to send you the results of these analyses.

_____

Ron Myers
U.S. Environmental Protection Agency
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Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
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**EMISSION MONITORING INC.**

EFFECTIVE SOLUTIONS AND ADVANCED TECHNOLOGIES

DATE: September 5, 2006

FROM: Roger T. Shigehara (Emission Monitoring Inc.)
Walter S. Smith (Walter S. Smith & Associates)

TO: Ron Meyers

SUBJECT: Method 202 Studies

Thank you for sending us an update. Based on the information you transmitted, it is obvious that the "dry" collection method is a superior approach to Method 202 by virtue of the fact that less water is involved. In addition, the preliminary results show 90% reduction at 25 ppm and 50% reduction at 150 ppm $SO_2$.

Walt Smith and I discussed your options. Our comments are as follows:

*Option 1: Maintaining the condenser and impinger before the cold filter at 68°F (20°C): Increasing the impinger inlet temperature reduces the amount of water collected, reduces the $SO_2$ in the water and may reduce the $SO_2$ conversion resulting in the condensate. For sources near ambient exhaust gas temperature, this modification will substantially reduce the collection of water. The final impinger and the silica gel trap will continue to be operated at ice bath temperature to ensure the moisture measurement is correct. We can not think of any significant downsides to this modification.*

Comment: We are assuming the temperature being monitored is the one before the cold filter and that the condenser could be operating at a higher temperature. Is there (±) figure around 68°F?

Your comment concerning "sources near ambient exhaust gas temperature" is true, but affects only a small category of sources. The majority of the sources involve combustion and thus high temperatures and moistures. The question is: Would operating at above ice-bath reduce the amount of $SO_2$ to a "tolerable" level at >10% moisture?

Another concern would be the effect of temperature on the organic fraction.

*Option 2: Adding acid to the first impinger to insure that the pH of the condensate is below 1.0: Two proposals were received, one is to use $H_2SO_4$ and the other is to use HCl. Both of these proposals would inhibit the conversion of $SO_2$ to $SO_3$. The use of $H_2SO_4$ would complicate the process of obtaining a condensable PM weight since the imprecision associated with the tare of the sulfuric acid would reduce the precision of the final weight of the condensable PM and may overshadow the $SO_3$ mass. The use of HCl has the benefit of evaporating completely with very low residue upon evaporation. The use of HCl in the presence of free ammonia in excess of the $SO_3$, $SO_2$ and $NO_x$ would create particulate ammonium chloride artifact that may exceed the artifact sulfate.*

Comment: We highly recommend the use of HCl.

*Option 3: Stabilizing a condensate aliquot and quantifying the sulfite: Glycerin could be*

*used to stabilize the sulfite and ion chromatography used to quantify the sulfite. The sulfite component would then be subtracted from the weighed mass. We do not have sufficient data to evaluate this option.*

Comment: We recommend that this be investigated for the benefit of the overall CPM lab experiment. The investigation should not be difficult to do. Bubble $SO_2$ gas directly from cylinder into water and add glycerin. If the sulfite concentration remains stable, the procedure works.

The subtraction procedure will be difficult to apply. The subtraction assumes that the sulfite content remains constant, i.e., is lost during the evaporation process. Adding an oxidizer to convert the sulfite to sulfate so that the proper amount of sulfite can be subtracted may complicate matters with other CPM.

Overall Comment and Recommendations:

The original purpose of CPM study was "to establish a baseline for M202 performance under the 'best' EPA recommended conditions" and to compare the results of M202 with that of the "dry" train. The definition of the "better" train is "a significantly lower number" than that of the other.

Obviously, the goal has changed. It is now, what can be done to lower the CPM artifact caused by $SO_2$ in the "dry" train. From your email report, we surmised that you came to the following conclusions:

- The 50% reduction at the 150-ppm $SO_2$ level makes the "dry" train results intolerable. The amount of CPM artifact is still too high.
- The amount of condensate collected in the knock-out impinger may affect the efficiency of purging. The normal GS impinger design is inadequate. The conclusion: more investigation on what design would be effective.
- Other options should be investigated.

So, we now ask, what can be done to reduce the $SO_2$ artifact? We know that the amount of $SO_2$ could be reduced by doing at least five things.

- Purge.
- Increase temperature.
- Reduce the amount of water used in the sampling train.
- Decrease the pH of the knock-out impinger (with HCl)
- Analyze sample for sulfates (assuming that $SO_3$ is the only inorganic condensable).

We recommend the following experiments:

**Experiment #1:**

The first experiment is to determine whether 0.01N HCl (or some other concentration) would effectively minimize the $SO_2$ absorption and, hence, the amount of CPM from $SO_2$ artifact. The procedure is as follows:

(1) Add 100 mL 0.01 N HCl into an impinger. Place in the ice bath.
(2) Bubble 150 ppm $SO_2$ at a rate of 0.5 scfm directly into the impinger until saturation (however long it took to saturate the solution with $SO_2$ in John Richard's experiments; as I remember, it didn't take that long).
(3) Analyze the solution with an ion chromatograph for sulfites and sulfates.
(4) Calculate the mg quantity of sulfites, sulfates, and total.
(5) If the 0.01N HCl solution works, then we need to look no further. We can stop

investigating the "dry" modified sampling train and concentrate on improving the Method 202 procedure with the use of 0.01N HCl. One improvement would be to reduce the amount of solution from 300 mL to perhaps 200, 150 mL or even 100 mL total.

(6) If the 0.01N HCl solution is marginally acceptable, repeat at the higher temperature of 68°F or go to step (7) and then repeat the experiment.
(7) If the 0.01N HCl solution doesn't work or is marginally effective, try the $N_2$ purge. To save time, an aliquot could be taken after step (2) and the rest of the sample could be purged.
(8) If the purge or the same experiment at 68°F temperature doesn't work or is marginally effective, go to Experiment #2.
(9) Note: A higher HCl concentration could also be investigated.

**Experiment #2:**

From the preliminary experiments, the "dry" train gave 50% reduction from that of Method 202 with the 150-ppm $SO_2$ gas. The "dry" train had about 37 mL condensate, and I am guessing that the Method 202 train had about 337 mL of liquid. Obviously, $SO_2$ dissolved in the moisture in the condensation coil, which then dripped to the knock-out impinger.

By now, you should have completed your investigation on whether the purging technique was the cause for the unacceptable reduction in artifact formation. If purging was effective, Experiment #2 need not be conducted and the use of 0.01N HCl need not be considered. However, if the purging is marginally acceptable, conduct the following to determine the effect of 0.01N HCl.

(1) Place 70 mL $H_2O$ in an impinger (amount of condensate for about 10% moisture stack) at room temperature (68°F) and bubble 150-ppm $SO_2$ gas until saturated.
(2) Take an aliquot of the solution and analyze for sulfites and sulfates.
(3) Add 50 mL of 0.01N HCl into the impinger.
(4) Take an aliquot of the solution and analyze for sulfites and sulfates.
(5) Purge the rest of the solution.
(6) At the end of the purge, analyze for sulfites and sulfates.

**Experiment #3:**

Only if the results show promise should the "dry" train be investigated further with the effect of $NH_3$. If $NH_3$ is present, then it would react with $SO_2$ in the condensation coil before it hits the acid solution. To determine the effect of $NH_3$, conduct the following experiment.

(1) Place 70 mL $H_2O$ in an impinger (amount of condensate for about 10% moisture stack) at room temperature (68°F) and bubble 150-ppm $SO_2$ gas and 10-pp, $NH_3$ gas for the same length of time as in Experiment #2.
(2) Take an aliquot of the solution and analyze for sulfites and sulfates.
(3) Add 50 mL of 0.01N HCl into the impinger.
(4) Take an aliquot of the solution and analyze for sulfites and sulfates.
(5) Purge the rest of the solution.
(6) At the end of the purge, analyze for sulfites and sulfates.

If a significant amount of sulfates are found, we have a problem and need to look at some other approach.

If you have any questions, please contact us.

8901 GLENWOOD AVENUE * RALEIGH, NC 27617-7503*PHONE (919) 781-3824*FAX (919) 782-9475

**From:** "Roger Shigehara" <rshigehara@mindspring.com> ***Index 5***
**To:** <Myers.Ron@epamail.epa.gov>, <PMUELLER@epri.com>, <Huntley.Roy@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Parker.Barrett@epamail.epa.gov>, <Westlin.Peter@epamail.epa.gov>, <Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov>, <Oldham.Conniesue@epamail.epa.gov>, <marksh@kochind.com>, <Sorrell.Candace@epamail.epa.gov>, <glenn.england@ge.com>, "'Garry Brooks'" <garry.brooks@erg.com>, "'John Richards'" <john.richards@aircontroltechniques.com>, <shannon.vogel@ncmail.net>, <Driscoll.Tom@epamail.epa.gov>, <ngoodman@epri.com>, "'Dominic Cianciarelli'" <Dominic.Cianciarelli@ec.gc.ca>, <hschiff@trcsolutions.com>, "'Joe Fanjoy'" <joe.fanjoy@erg.com>, <Hardin.Erik@epamail.epa.gov>, <seebea@dnr.state.wi.us>, <mstewartdouglas@4cleanair.org>, "'Karl Loos'" <karl.loos@shell.com>, "'Roy Owens'" <roy.owens@owenscorning.com>, <frank.jarke@ps.ge.com>, <cglowacki@technikonllc.com>, <DCLINE@dem.state.in.us>, <Segall.Robin@epamail.epa.gov>, "'Bill Walker'" <bwalker@cleanair.com>, "'Walt Smith'" <walt@waltersmith.com>, <LSRitts@HHLAW.com>, "'Christopher Van Atten'" <vanatten@mjbradley.com>, "'Randy Bower'" <randy.bower@erg.com>, "'Michael Palazzolo'" <michael.palazzolo@alcoa.com>, "'Jerry Fulmer'" <jbfulmer@aol.com>, "'Jeffrey Lettrich'" <jeffrey.lettrich@alcoa.com>, "'Patricia Strabbing'" <pas2@daimlerchrysler.com>, "'Mary Snow-Cooper'" <ms14@daimlerchrysler.com>, "'Kathleen Hennessey'" <kmh17@daimlerchrysler.com>, "'Debby Rowe'" <das24@daimlerchrysler.com>, "'Marc Deslauriers'" <Marc.Deslauriers@ec.gc.ca>, <Shine.Brenda@epamail.epa.gov>, "'Bruce Steiner'" <BruceS@steel.org>, "'Steve McDaniel'" <asmcdaniel@aqm.co.knox.tn.us>, "'Mark Lutrzkowski'" <Mark.Lutrzykowski@state.de.us>, "'Jeff Hege'" <jhege@indygov.org>, <linak.bill@epamail.epa.gov>, "'Danny Greene'" <Danny.Greene@erg.com>, "'Joseph Martini'" <joseph.martini@state.de.us>, "'Jeffrey Rogers'" <jeffrey.rogers@state.de.us>, <Gary.Helm@Conectiv.com>, <wreistad@tristategt.org>, <ValmontH@kochind.com>, <George.Marson@ec.gc.ca>, "'Cory Wind'" <wind.cory@deq.state.or.us>, "'Ralph Roberson'" <roberson@rmb-consulting.com>, <Foley.Patrick@epamail.epa.gov>, <Krishna.Row@fhr.com>, <wrp6@daimlerchrysler.com>, <Ray.Merrill@erg.com>, <BOConnor@paprican.ca>, <lfreeman@hunton.com>, <l_carlson@src-ncasi.org>, "'Ashok Jain'" <AJain@src-ncasi.org>, <drhoades@cleanair.com>, <jchaffee@bison-eng.com>
**Date:** Wed, Sep 6, 2006 9:17 AM
**Subject:** RE: Update of Condensable PM test method improvement project.

Ron,
I emailed this last night, but got a lot of returns. So I'm resending our comments.

Roger

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Thursday, August 31, 2006 5:40 PM
To: PMUELLER@epri.com; Huntley.Roy@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Westlin.Peter@epamail.epa.gov; Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov; Oldham.Conniesue@epamail.epa.gov; marksh@kochind.com; Sorrell.Candace@epamail.epa.gov; glenn.england@ge.com; Garry Brooks; John Richards; shannon.vogel@ncmail.net; Driscoll.Tom@epamail.epa.gov; ngoodman@epri.com; Dominic Cianciarelli; hschiff@trcsolutions.com; Joe Fanjoy; Hardin.Erik@epamail.epa.gov; seebea@dnr.state.wi.us; mstewartdouglas@4cleanair.org; Karl Loos; Roy Owens; frank.jarke@ps.ge.com; cglowacki@technikonllc.com; DCLINE@dem.state.in.us; Segall.Robin@epamail.epa.gov; Bill Walker; Walt Smith; LSRitts@HHLAW.com; Christopher Van Atten; Randy Bower; Michael Palazzolo; Jerry Fulmer; Jeffrey Lettrich; Patricia Strabbing; Mary Snow-Cooper; Kathleen Hennessey; Debby Rowe; Marc Deslauriers; Shine.Brenda@epamail.epa.gov; Bruce Steiner; Steve

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Subject: Update of Condensable PM test method improvement project.

Condensable PM test method improvement stakeholders:

It has been too long since I have updated you on the progress (or lack thereof) of our exploratory analyses. We have encountered a procedural anomaly with the dry impinger modification to Method 202 that we are solving. We found sulfate concentrations in dry impinger samples were 90% reduced from the standard Method 202 results at 25 ppm SO2 concentration. At higher SO2 (150 ppm) we only found a 50% reduction in the sulfate. Our belief entering this project was that the dry impinger method reduction in the artifact would be independent of SO2 concentration in our experimental matrix. The cause of this situation may be poor sparging because the modified Greenberg Smith impinger insert did not reach into the final water volume (37 ml) to force nitrogen through the liquid. We believe that by using impinger inserts that enter the collected condensate we will achieve sparging consistent with the lower SO2 tests. We may replicate one or more of the dry impinger samples using an impinger nozzle that is longer and improves the sparging of the collected water.

On another topic, during our workshop there were several suggestions on simple techniques that we might use to reduce further the SO2 artifact formation. We are considering including these in the plan and evaluating some or all of them in the EPA laboratory experiments. The techniques that we believe offer some advantages include:

Maintaining the condenser and impinger before the cold filter at 68 ºF (20 ºC): Increasing the impinger inlet temperature reduces the amount of water collected, reduces the SO2 in the water and may reduce the SO2 conversion resulting in the condensate. For sources near ambient exhaust gas temperature, this modification will substantially reduce the collection of water. The final impinger and the silica gel trap will continue to be operated at ice bath temperature to ensure the moisture measurement is correct. We can not think of any significant downsides to this modification.

Adding acid to the first impinger to insure that the pH of the condensate is below 1.0: Two proposals were received, one is to use H2SO4 and the other is to use HCl. Both of these proposals would inhibit the conversion of SO2 to SO3. The use of H2SO4 would complicate the process of obtaining a condensable PM weight since the imprecision associated with the tare of the sulfuric acid would reduce the precision of the final weight of the condensable PM and may overshadow the SO3 mass. The use of HCl has the benefit of evaporating completely with very low residue upon evaporation. The use of HCl in the presence of free ammonia in excess of the SO3, SO2 and NOx would create particulate ammonium chloride artifact that may

exceed the artifact sulfate.

Stabilizing a condensate aliquot and quantifying the sulfite: Glycerin could be used to stabilize the sulfite and ion chromatography used to quantify the sulfite. The sulfite component would then be subtracted from the weighed mass. We do not have sufficient data to evaluate this option.

We would like additional input on the potential advantages and disadvantages of these three options. We would appreciate this additional input by Monday September 11 so we can procede with the completion of the plan and begin the EPA laboratory assessments.

Thank you,

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

**EMISSION MONITORING INC.**

EFFECTIVE SOLUTIONS AND ADVANCED TECHNOLOGIES

DATE: September 5, 2006

FROM: Roger T. Shigehara (Emission Monitoring Inc.)
Walter S. Smith (Walter S. Smith & Associates)

TO: Ron Meyers

SUBJECT: Method 202 Studies

Thank you for sending us an update. Based on the information you transmitted, it is obvious that the "dry" collection method is a superior approach to Method 202 by virtue of the fact that less water is involved. In addition, the preliminary results show 90% reduction at 25 ppm and 50% reduction at 150 ppm $SO_2$.

Walt Smith and I discussed your options. Our comments are as follows:

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Your comment concerning "sources near ambient exhaust gas temperature" is true, but affects only a small category of sources. The majority of the sources involve combustion and thus high temperatures and moistures. The question is: Would operating at above ice-bath reduce the amount of $SO_2$ to a "tolerable" level at >10% moisture?

Another concern would be the effect of temperature on the organic fraction.

*Option 2: Adding acid to the first impinger to insure that the pH of the condensate is below 1.0: Two proposals were received, one is to use $H_2SO_4$ and the other is to use HCl. Both of these proposals would inhibit the conversion of $SO_2$ to $SO_3$. The use of $H_2SO_4$ would complicate the process of obtaining a condensable PM weight since the imprecision associated with the tare of the sulfuric acid would reduce the precision of the final weight of the condensable PM and may overshadow the $SO_3$ mass. The use of HCl has the benefit of evaporating completely with very low residue upon evaporation. The use of HCl in the presence of free ammonia in excess of the $SO_3$, $SO_2$ and $NO_x$ would create particulate ammonium chloride artifact that may exceed the artifact sulfate.*

Comment: We highly recommend the use of HCl.

*Option 3: Stabilizing a condensate aliquot and quantifying the sulfite: Glycerin could be*

*used to stabilize the sulfite and ion chromatography used to quantify the sulfite. The sulfite component would then be subtracted from the weighed mass. We do not have sufficient data to evaluate this option.*

Comment: We recommend that this be investigated for the benefit of the overall CPM lab experiment. The investigation should not be difficult to do. Bubble $SO_2$ gas directly from cylinder into water and add glycerin. If the sulfite concentration remains stable, the procedure works.

The subtraction procedure will be difficult to apply. The subtraction assumes that the sulfite content remains constant, i.e., is lost during the evaporation process. Adding an oxidizer to convert the sulfite to sulfate so that the proper amount of sulfite can be subtracted may complicate matters with other CPM.

Overall Comment and Recommendations:

The original purpose of CPM study was "to establish a baseline for M202 performance under the 'best' EPA recommended conditions" and to compare the results of M202 with that of the "dry" train. The definition of the "better" train is "a significantly lower number" than that of the other.

Obviously, the goal has changed. It is now, what can be done to lower the CPM artifact caused by $SO_2$ in the "dry" train. From your email report, we surmised that you came to the following conclusions:

- The 50% reduction at the 150-ppm $SO_2$ level makes the "dry" train results intolerable. The amount of CPM artifact is still too high.
- The amount of condensate collected in the knock-out impinger may affect the efficiency of purging. The normal GS impinger design is inadequate. The conclusion: more investigation on what design would be effective.
- Other options should be investigated.

So, we now ask, what can be done to reduce the $SO_2$ artifact? We know that the amount of $SO_2$ could be reduced by doing at least five things.

- Purge.
- Increase temperature.
- Reduce the amount of water used in the sampling train.
- Decrease the pH of the knock-out impinger (with HCl)
- Analyze sample for sulfates (assuming that $SO_3$ is the only inorganic condensable).

We recommend the following experiments:

**Experiment #1:**

The first experiment is to determine whether 0.01N HCl (or some other concentration) would effectively minimize the $SO_2$ absorption and, hence, the amount of CPM from $SO_2$ artifact. The procedure is as follows:

(1) Add 100 mL 0.01 N HCl into an impinger. Place in the ice bath.
(2) Bubble 150 ppm $SO_2$ at a rate of 0.5 scfm directly into the impinger until saturation (however long it took to saturate the solution with $SO_2$ in John Richard's experiments; as I remember, it didn't take that long).
(3) Analyze the solution with an ion chromatograph for sulfites and sulfates.
(4) Calculate the mg quantity of sulfites, sulfates, and total.
(5) If the 0.01N HCl solution works, then we need to look no further. We can stop

investigating the "dry" modified sampling train and concentrate on improving the Method 202 procedure with the use of 0.01N HCl. One improvement would be to reduce the amount of solution from 300 mL to perhaps 200, 150 mL or even 100 mL total.

(6) If the 0.01N HCl solution is marginally acceptable, repeat at the higher temperature of 68°F or go to step (7) and then repeat the experiment.
(7) If the 0.01N HCl solution doesn't work or is marginally effective, try the $N_2$ purge. To save time, an aliquot could be taken after step (2) and the rest of the sample could be purged.
(8) If the purge or the same experiment at 68°F temperature doesn't work or is marginally effective, go to Experiment #2.
(9) Note: A higher HCl concentration could also be investigated.

**Experiment #2:**

From the preliminary experiments, the "dry" train gave 50% reduction from that of Method 202 with the 150-ppm $SO_2$ gas. The "dry" train had about 37 mL condensate, and I am guessing that the Method 202 train had about 337 mL of liquid. Obviously, $SO_2$ dissolved in the moisture in the condensation coil, which then dripped to the knock-out impinger.

By now, you should have completed your investigation on whether the purging technique was the cause for the unacceptable reduction in artifact formation. If purging was effective, Experiment #2 need not be conducted and the use of 0.01N HCl need not be considered. However, if the purging is marginally acceptable, conduct the following to determine the effect of 0.01N HCl.

(1) Place 70 mL $H_2O$ in an impinger (amount of condensate for about 10% moisture stack) at room temperature (68°F) and bubble 150-ppm $SO_2$ gas until saturated.
(2) Take an aliquot of the solution and analyze for sulfites and sulfates.
(3) Add 50 mL of 0.01N HCl into the impinger.
(4) Take an aliquot of the solution and analyze for sulfites and sulfates.
(5) Purge the rest of the solution.
(6) At the end of the purge, analyze for sulfites and sulfates.

**Experiment #3:**

Only if the results show promise should the "dry" train be investigated further with the effect of $NH_3$. If $NH_3$ is present, then it would react with $SO_2$ in the condensation coil before it hits the acid solution. To determine the effect of $NH_3$, conduct the following experiment.

(1) Place 70 mL $H_2O$ in an impinger (amount of condensate for about 10% moisture stack) at room temperature (68°F) and bubble 150-ppm $SO_2$ gas and 10-pp, $NH_3$ gas for the same length of time as in Experiment #2.
(2) Take an aliquot of the solution and analyze for sulfites and sulfates.
(3) Add 50 mL of 0.01N HCl into the impinger.
(4) Take an aliquot of the solution and analyze for sulfites and sulfates.
(5) Purge the rest of the solution.
(6) At the end of the purge, analyze for sulfites and sulfates.

If a significant amount of sulfates are found, we have a problem and need to look at some other approach.

If you have any questions, please contact us.

8901 GLENWOOD AVENUE * RALEIGH, NC 27617-7503*PHONE (919) 781-3824*FAX (919) 782-9475

**From:** "Goodman, Naomi" <Ngoodman@epri.com> ***Index 6***
**To:** <Myers.Ron@epamail.epa.gov>, <PMUELLER@epri.com>, <Huntley.Roy@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Parker.Barrett@epamail.epa.gov>, <Westlin.Peter@epamail.epa.gov>, <Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov>, <Oldham.Conniesue@epamail.epa.gov>, <marksh@kochind.com>, <Sorrell.Candace@epamail.epa.gov>, <glenn.england@ge.com>, "Garry Brooks" <garry.brooks@erg.com>, "John Richards" <john.richards@aircontroltechniques.com>, <shannon.vogel@ncmail.net>, <Driscoll.Tom@epamail.epa.gov>, "Dominic Cianciarelli" <Dominic.Cianciarelli@ec.gc.ca>, <hschiff@trcsolutions.com>, "Joe Fanjoy" <joe.fanjoy@erg.com>, <Hardin.Erik@epamail.epa.gov>, <seebea@dnr.state.wi.us>, <mstewartdouglas@4cleanair.org>, "Karl Loos" <karl.loos@shell.com>, "Roy Owens" <roy.owens@owenscorning.com>, <frank.jarke@ps.ge.com>, <cglowacki@technikonllc.com>, <DCLINE@dem.state.in.us>, <Segall.Robin@epamail.epa.gov>, "Bill Walker" <bwalker@cleanair.com>, "Walt Smith" <walt@waltersmith.com>, <LSRitts@HHLAW.com>, "Christopher Van Atten" <vanatten@mjbradley.com>, "Randy Bower" <randy.bower@erg.com>, "Michael Palazzolo" <michael.palazzolo@alcoa.com>, "Jerry Fulmer" <jbfulmer@aol.com>, "Jeffrey Lettrich" <jeffrey.lettrich@alcoa.com>, "Patricia Strabbing" <pas2@daimlerchrysler.com>, "Mary Snow-Cooper" <ms14@daimlerchrysler.com>, "Kathleen Hennessey" <kmh17@daimlerchrysler.com>, "Debby Rowe" <das24@daimlerchrysler.com>, "Marc Deslauriers" <Marc.Deslauriers@ec.gc.ca>, <Shine.Brenda@epamail.epa.gov>, "Bruce Steiner" <BruceS@steel.org>, "Steve McDaniel" <asmcdaniel@aqm.co.knox.tn.us>, "Mark Lutrzkowski" <Mark.Lutrzykowski@state.de.us>, "Jeff Hege" <jhege@indygov.org>, <linak.bill@epamail.epa.gov>, "Danny Greene" <Danny.Greene@erg.com>, "Joseph Martini" <joseph.martini@state.de.us>, "Jeffrey Rogers" <jeffrey.rogers@state.de.us>, <Gary.Helm@Conectiv.com>, <wreistad@tristategt.org>, <ValmontH@kochind.com>, <George.Marson@ec.gc.ca>, "Cory Wind" <wind.cory@deq.state.or.us>, <rshigehara@mindspring.com>, "Ralph Roberson" <roberson@rmb-consulting.com>, <Foley.Patrick@epamail.epa.gov>, <Krishna.Row@fhr.com>, <wrp6@daimlerchrysler.com>, <Ray.Merrill@erg.com>, <BOConnor@paprican.ca>, <lfreeman@hunton.com>, <l_carlson@src-ncasi.org>, "Ashok Jain" <AJain@src-ncasi.org>, <drhoades@cleanair.com>, <jchaffee@bison-eng.com>
**Date:** Wed, Sep 6, 2006 5:40 PM
**Subject:** RE: Update of Condensable PM test method improvement project.

Ron;

My comments on your proposed additions to the July 14 Laboratory Test Plan are as follows:

1. Use of a 68F (20C) temperature in the condenser and first dry impinger.

This is a logical approach, but it may be awkward to apply in practice. You would need separate cooling systems for the first impinger and for the impingers after the filter. This goes against your goal to use standard glassware and equipment. However, that is not a major obstacle.

Please clarify whether the condenser temparature will change with this addition. The test plan doesn't specify a condenser temperature but the Richards et al. paper on which you based the dry impinger method cites "below 68F".

How much volume would you expect the impingers after the filter to collect at low (5%) and high (15%) moisture conditions? Depending on the volume of water, you could still get a significant artifact from SO2 dissolved in the second and third impingers.

2. Addition of H2SO4 or HCl to the first dry impinger

The addition of sulfuric acid does not make sense. As you note, the inaccuracy in the weight of added acid could overwhelm the actual CPM measurement. Adding HCl is worth attempting, but as you point out, will work only for sources that do not have free ammonia. Note that ammonia solubility increases at low pH, so the potential for ammonium chloride artifact formation would be greater for a given concentration of

gaseous ammonia.

One concern with this approach is what the pH adjustment would do to organic condensibles. I'm not familiar with the reactions involved in formation of organic CPM bias, but phenols can react with NOx at very low pH to form nitrophenols. If there are further aqueous condensation reactions, you could be creating artifactual organic CPM.

3. Stabilization of sulfite/sulfate ratios with glycerol

The purpose of stabilizing the ratio is not clear to me. EPRI research also indicates that the pre-evaporation impinger liquid can contain sulfites, but that the sulfite is completely converted to sulfate during evaporation of the impinger residue. Since the evaporation step is part of Method 202, and is also part of the dry impinger technique, it is irrelevant which species is present in the impinger. The distinction is only important if ion chromatography of the nonevaporated impinger water is used to quantify CPM, rather than a gravimetric technique. In addition, subtraction of sulfite from CPM is probably not appropriate, since sulfite will react quickly with moisture or NOx in the atmosphere to form sulfuric acid.

If you want to determine the ratio for research purposes, in order to better understand the chemistry occuring in the impingers, the approach you have suggested is reasonable.

As a general comment, you invited stakeholders to suggest additional tests that they would be interested in funding. Several organizations, including EPRI, indicated an interest in this at the stakeholders meeting. If this is going to happen, there needs to be a conversation among the stakeholders, and with EPA, to determine the scope of the tests and the timeframe for conducting those tests. I would appreciate if any stakeholders with an interest in supplementing EPA's efforts contact me to determine if there are common areas of interest.

Naomi Goodman

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Condensable PM test method improvement stakeholders:

It has been too long since I have updated you on the progress (or lack thereof) of our exploratory analyses. We have encountered a procedural anomaly with the dry impinger modification to Method 202 that we are solving. We found sulfate concentrations in dry impinger samples were 90% reduced from the standard Method 202 results at 25 ppm SO2 concentration. At higher SO2 (150 ppm) we only found a 50% reduction in the sulfate. Our belief entering this project was that the dry impinger method reduction in the artifact would be independent of SO2 concentration in our experimental matrix. The cause of this situation may be poor sparging because the modified Greenberg Smith impinger insert did not reach into the final water volume (37 ml) to force nitrogen through the liquid. We believe that by using impinger inserts that enter the collected condensate we will achieve sparging consistent with the lower SO2 tests. We may replicate one or more of the dry impinger samples using an impinger nozzle that is longer and improves the sparging of the coll ected water.

On another topic, during our workshop there were several suggestions on simple techniques that we might use to reduce further the SO2 artifact formation. We are considering including these in the plan and evaluating some or all of them in the EPA laboratory experiments. The techniques that we believe offer some advantages include:

Maintaining the condenser and impinger before the cold filter at 68 ºF (20 ºC): Increasing the impinger inlet temperature reduces the amount of water collected, reduces the SO2 in the water and may

reduce the SO2 conversion resulting in the condensate. For sources near ambient exhaust gas temperature, this modification will substantially reduce the collection of water. The final impinger and the silica gel trap will continue to be operated at ice bath temperature to ensure the moisture measurement is correct. We can not think of any significant downsides to this modification.

Adding acid to the first impinger to insure that the pH of the condensate is below 1.0: Two proposals were received, one is to use H2SO4 and the other is to use HCl. Both of these proposals would inhibit the conversion of SO2 to SO3. The use of H2SO4 would complicate the process of obtaining a condensable PM weight since the imprecision associated with the tare of the sulfuric acid would reduce the precision of the final weight of the condensable PM and may overshadow the SO3 mass. The use of HCl has the benefit of evaporating completely with very low residue upon evaporation. The use of HCl in the presence of free ammonia in excess of the SO3, SO2 and NOx would create particulate ammonium chloride artifact that may exceed the artifact sulfate.

Stabilizing a condensate aliquot and quantifying the sulfite: Glycerin could be used to stabilize the sulfite and ion chromatography used to quantify the sulfite. The sulfite component would then be subtracted from the weighed mass. We do not have sufficient data to evaluate this option.

We would like additional input on the potential advantages and disadvantages of these three options. We would appreciate this additional input by Monday September 11 so we can procede with the completion of the plan and begin the EPA laboratory assessments.

Thank you,

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards Sector Policy and Programs Division Monitoring Policy Group, D243-05 RTP NC 27711 Tel. 919.541.5407 Fax 919.541.1039 E-mail myers.ron@epa.gov

**From:** "Clifford Glowacki" <cglowacki@technikonllc.com> ***Index 7***
**To:** <Myers.Ron@epamail.epa.gov>
**Date:** Mon, Sep 11, 2006 11:23 AM
**Subject:** RE: Update of Condensable PM test method improvement project.

Ron,

I have been following the comments from Roger and Naomi and believe that the higher temperature and addition of HCl are good modifications. The only caution I have is that by raising the temperature the rate of conversion of SO2 to SO3 and then to SO4 will be increased and purging after the run will be less effective.

Cliff

Clifford R. Glowacki, CIH
Vice President - Measurement Technologies
Phone: 614-873-0609
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Cell: 614-371-8666

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Thursday, August 31, 2006 5:40 PM
To: PMUELLER@epri.com; Huntley.Roy@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Westlin.Peter@epamail.epa.gov; Gary_McAlister/RTP/USEPA/US@mintra01.rtp.epa.gov; Oldham.Conniesue@epamail.epa.gov; marksh@kochind.com; Sorrell.Candace@epamail.epa.gov; glenn.england@ge.com; Garry Brooks; John Richards; shannon.vogel@ncmail.net; Driscoll.Tom@epamail.epa.gov; ngoodman@epri.com; Dominic Cianciarelli; hschiff@trcsolutions.com; Joe Fanjoy; Hardin.Erik@epamail.epa.gov; seebea@dnr.state.wi.us; mstewartdouglas@4cleanair.org; Karl Loos; Roy Owens; frank.jarke@ps.ge.com; Clifford Glowacki; DCLINE@dem.state.in.us; Segall.Robin@epamail.epa.gov; Bill Walker; Walt Smith; LSRitts@HHLAW.com; Christopher Van Atten; Randy Bower; Michael Palazzolo; Jerry Fulmer; Jeffrey Lettrich; Patricia Strabbing; Mary Snow-Cooper; Kathleen Hennessey; Debby Rowe; Marc Deslauriers; Shine.Brenda@epamail.epa.gov; Bruce Steiner; Steve McDaniel; Mark Lutrzkowski; Jeff Hege; linak.bill@epamail.epa.gov; Danny Greene; Joseph Martini; Jeffrey Rogers; Gary.Helm@Conectiv.com; wreistad@tristategt.org; ValmontH@kochind.com; George.Marson@ec.gc.ca; Cory Wind; rshigehara@mindspring.com; Ralph Roberson; Foley.Patrick@epamail.epa.gov; Krishna.Row@fhr.com; wrp6@daimlerchrysler.com; Ray.Merrill@erg.com; BOConnor@paprican.ca; lfreeman@hunton.com; l_carlson@src-ncasi.org; Ashok Jain; drhoades@cleanair.com; jchaffee@bison-eng.com
Subject: Update of Condensable PM test method improvement project.

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nitrogen through the liquid. We believe that by using impinger inserts that enter the collected condensate we will achieve sparging consistent with the lower SO2 tests. We may replicate one or more of the dry impinger samples using an impinger nozzle that is longer and improves the sparging of the collected water.

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Thank you,

_____

Ron Myers
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***Index 8***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** <Ray.Merrill@erg.com>
**Date:** Mon, Sep 11, 2006 4:17 PM
**Subject:** Method 202 runs

Hi Ray,

Please find attached a summary on my notes on the latest Method 202 runs.

Regards

George Marson, P.Eng.

QA & EMS Supervisor

phone (613) 991-9458

fax (613) 998-4032

# PRELIMINARY RESULTS WITH "DRY IMPINGER" METHOD 202

## 1.0 Sampling

Fifteen (15) Method 202 laboratory runs were performed with conventional stack testing equipment. Ambient air was aspirated trough a 3" glass fiber filter and then humidified by bubbling through a water impinger housed within the oven of a Method 5 sampling train. This impinger was fitted with a 250 w heating tape which was powered from an adjustable rheostat. Moisture levels were varied by altering the oven temperature as well as the power to the heating tape.

An analyzed mixture of $SO_2$ in nitrogen (2,000 to 4,000 ppm) was added at constant rate to the moisturized air stream. The $SO_2$ flow started approximately 15 seconds after the start of the air flow and was stopped 15 seconds before the end of the 1 hr run.

The sampling train consisted of a water-cooled coil, a condensate reservoir ("dry impinger"), a strait stem impinger, and a silica gel impinger. All these components were kept at ice bath temperature, except the condensate reservoir which was external to the ice box.

The sampling train was linked to the corresponding control module and operated at a rate of approximately 0.6 scfm. Approximately 94% of the moisture gain was collected in the "dry impinger", 1% in the second impinger and the balance in the silica gel impinger.

## 2.0 Nitrogen purging

At the completion of each run, the condensate was transferred to a Greenburg-Smith impinger and it was purged at room temperature with a total of 1.2 $Sm^3$ of nitrogen (Praxair, ultra high purity) over 1 hour. Black CPM residue was observed on some preliminary runs, so a 47 mm glass fiber filter was installed in the low pressure nitrogen line and in the $SO_2$ mixture line. Black CPM residue was not encountered on subsequent test runs.

## 3.0 Evaporation and Weighing of Inorganic CPM

Method 202 requires the evaporation of considerable amounts of water and the gravimetric determination of the evaporation residue. Even in the case of the proposed "dry impingers" version of Method 202, it is necessary to evaporate approximately 200 ml for a 1hr test run on a 20% moisture source. The samples are placed in glass containers and dried in an oven set at 105 deg. C.

The determination of residue may follow two main alternatives:

a) Direct residue determination in the same glass container where evaporation was carried out
b) Drying in large glass containers followed by wet transfer to a weighing pan and a second drying step

Alternative a) is simple from the point of view of residue manipulation, but it is quite demanding regarding the precision weighing of bulky glass containers. In our investigation, the evaporation/drying jars were pre-cleaned 120 ml and 250 ml clear wide mouth jars (EP Scientific Products) which weighed approximately 114 g and 204 g, respectively. The jars had a glass volume of 44 ml and 78 ml, assuming 2.6 g/l glass density. The scale had 210 g capacity, 0.0001 g readability and 2.5ppm/$^{o}$C sensitivity drift (Mettler-Toledo AL204).

Taring of the empty glass containers is required two or more days prior to the weighing of the evaporation residues. Weighing room pressure and temperature may not be exactly the same. The effect of common environmental differences on the apparent weight of the 250 ml jars was estimated as follows:

Effect of 1 kPa lab pressure change:

1 kPa/101.3 kPa*0.0012 g/ml *78 ml = 0.9 mg, due to air buoyancy

Effect of 1 $^{o}$C lab temperature change:

1$^{o}$C*2.5ppm per $^{o}$C/1,000,000 *204 g = 0.6 mg, due to scale thermal sensitivity drift

Several weighing experiments were carried out to confirm the shortcomings of conventional "weight-before-and-after" approach for the determination of inorganic CPM in glass jars.

Four (4) sets of 24 jars each were weighed in a given order 6 times over a 4 day period. The average weight of each jar had a standard deviation of 0.5 mg. However, the average weight differences of consecutive jars had a standard deviation of 0.2 mg. This appears due to the fact that the environmental conditions during the weighing of consecutive jars were more consistent than the conditions from weighing the same jar on different days.

It was also observed that the 0.5 mg consistency criterion for acceptance of consecutive weightings was often exceeded, even though the weight was stable with respect to the preceding glass jar. This criterion may be suitable for filters but it is inadequate for bulky glass jars.

Based on these observations, an alternate weighing scheme was adopted for the condensable particulate matter (CPM) samples. Prior to running Method 202 experiments a set of weighing jars were tared by multiple weightings >=6 hours apart, which were < 0.5 mg from each other. Each time the jars were weighted in the same order. Every other jar in the set was used to contain and evaporate the samples. The remaining jars stayed empty and served as reference for the jar that in the set was weighted immediately before or after. In this manner the above mentioned effects were compensated for, at least in what is associated to the bulky weighing containers.

The average standard deviation resulting from weighing multiple inorganic CPM samples in this manner was estimated to be 0.2 mg.

The multiple weighing experiment was also performed on aluminum weighing pans, using the same equipment.

The effect of common environmental differences on the apparent weight of the weighing pans was estimated as follows:

Effect of 1 kPa lab pressure change
1 kPa/101.3 kPa*0.0012 g/ml *0.44 ml = 0.005 mg, due to air buoyancy

Effect of 1 $^{o}$C lab temperature change
1$^{o}$C*2.5ppm per $^{o}$C/1,000,000 *1.2 g = 0.003 mg, due to scale thermal sensitivity drift

The effects are much lower than the readability of the scale used (0.1 mg). In this respect, weighing alternative b) appears to be more favorable than alternative a). It remains to be determined, however, that: 1) the CPM can be transferred quantitatively from the drying jars, and 2) that no artifact results from the interaction of the transferred liquid with the aluminum foil.

The residues of 15 Method 202 laboratory runs were transferred into 1.2 g aluminum pans by 3 successive rinses, each with 2 ml DI water. In some runs (1 to 10), the condensate was evenly split into 2 jars, therefore the total water volume loaded into the weighing pans was approximately 12 ml. The tared weighing pans were dried overnight. Tare and final weighing was the average of 3 consecutive determinations >=6 hours apart, which were < 0.5 mg from each other.

The average standard deviation resulting from weighing multiple inorganic CPM samples in this manner was estimated to be 0.1 mg.

The results from 15 Method 202 laboratory runs (inorganic CPM determinations) are summarized in Table 1.

**Table 1**
**Results Summary**

| Test run No. | 1 | 2 | 3 | 4 | 5 | **Avg.** | Std. dev. | Notes |
|---|---|---|---|---|---|---|---|---|
| CPM, mg/Dm3 | 2.8 | 1.0 | 1.0 | 1.1 | 2.5 | **1.7** | 0.9 | pan weighing |
| CPM, mg/Dm3 | 4.1 | 1.5 | 1.4 | 1.4 | 2.0 | **2.1** | 1.2 | jar weighing |
| Moisture, % | 12.7% | 11.1% | 11.2% | 11.3% | 11.2% | **11.5%** | 0.7% | |
| SO2, ppmd | 253 | 252 | 255 | 258 | 258 | **255** | 2.9 | |
| | | | | | | | | |
| Test run No. | 6 | 7 | 8 | 9 | 10 | | | |
| CPM, mg/Dm3 | 1.9 | 0.9 | 1.0 | 0.8 | 0.8 | **1.1** | 0.4 | pan weighing |
| CPM, mg/Dm3 | 3.1 | 0.5 | 1.3 | 1.5 | 1.0 | **1.5** | 1.0 | jar weighing |
| Moisture, % | 12.3% | 11.8% | 11.7% | 11.6% | 10.8% | **11.7%** | 0.5% | |
| SO2, ppmd | 25 | 25 | 25 | 25 | 25 | **25** | 0.2 | |
| | | | | | | | | |
| Test run No. | 11 | 12 | 13 | 14 | 15 | | | |
| CPM, mg/Dm3 | 2.4 | 0.9 | 0.7 | 0.9 | 2.0 | **1.1** | 0.7 | pan weighing |
| Moisture, % | 20.8% | 19.7% | 19.5% | 19.8% | 21.0% | **11.7%** | 0.7% | |
| SO2, ppmd | 123 | 121 | 121 | 121 | 122 | **121** | 1.1 | |

## 5.0 Sample Storage

In this scouting test program the liquid samples were dried a few hours after the test runs. It is acknowledged that sulfites remaining in the condensate after the nitrogen purge may oxidize during longer storage and hence produce additional inorganic CPM. To investigate this potential contribution to inorganic CPM formation, the condensate from test runs 1 to 10 was split in two halves, one of which was spiked with 3 drops of 30% $H_2O_2$ (approximately 0.15 ml). The peroxide spike would oxidize instantaneously any residual sulfite. Subsequent evaporation and jar weighing determined that the spiked jars contained on average 0.4 mg higher CPM than the unspiked jars. This rather modest increase provides an upper bound indication of potential CPM formation upon extended sample storage.

## 6.0 Observations and Comments

- The inorganic CPM artifact caused by SO2 may be reduced to approximately 2 mg or less by the proposed “dry impinger” version of Method 202.
- A ten fold increase in $SO_2$ level caused only a modest increase in inorganic CPM artifact.
- Nitrogen gas volume is similar to the sample volume, and should be filtered to the same extent.
- The drying and weighing of condensate on the same glass jars requires special consideration to the effects of changes in atmospheric pressure and weighing room temperature
- The quantitative transfer of redissolved condensate to weighing pans should be described in the method

- Nitrogen purge at ambient temperature is likely to be more effective than the prescribed purge at ice bath temperature

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca> ***Index 9***
**To:** <ray.merrill@erg.com>
**Date:** Mon, Sep 18, 2006 9:15 AM
**Subject:** FW: Method 202

Hi Ray:

As I commented to you earlier, I started a scouting experiment on the storage of Method 201 samples prior to analysis. It is based on two sets of 4 jars each containing approximately 250 ml of degassed SO2-water solution (no headspace), and a third set containing 200ml of the same solution and 50 ml of air headspace. One jar per set will be opened and evaporated after 2 days, 4 days, and 8 days of fridge storage. The last jar of the set will be spiked with H2O2 to simulate lenghtier storage. The no-headspace storage of the nitrogen-purged Method 202 condensate appears to be the most direct way to prevent artifact growth prior to lab analysis. I would only require degassed DI water to top up the voume of the actual samples.

In parallel to it, I have looked at O2 scavengers for boiler water that may be used as an alternate to the no-headspace storage. In so doing , I came across an article (attached) that compared the reactivity of various boiler water additives at room temperature . Sulfite is the fastest O2 scavenger at room temperature. At pH >= 8 sulphite reduces the dissolved O2 level to half the original level in about one minute!. Fortunately we know that at lower pH bisulphite is much slower, otherwise the Method 202 artifact would be enormous.

Two observations: 1) the ammonia neutralization of condensate that you favour, should be carried out immediately after sample degassing or on a little volume of redissolved evaporation residue, otherwise the rising pH will ensure the reaction of any dissolved O2 in the liquid (which then becomes 6 times as much CPM artifact). 2) Given the reactivity of sulfite, Method 202 is in big trouble if a source have less SO2 than ammonia slip, so that the condensate es neutral or alkaline.

Regards

PS. N-N-diethylhydroxylamine (DEHA) appears to be a good candidate O2 scavenger to preserve the samples (volatile and reasonably reactive at ambient temperature). I plan a scouting test with it as soon as I receive it from Aldrich.

**TECHNICAL LITERATURE (1)**

# OXYGEN SCAVENGERS
# For Boiler Water Treatment

Corrosion by oxygen in the boiler can be controlled by the addition of an "oxygen scavenger" to the preboiler section of the steam generating system. It is generally fed, along with other treatment chemicals, as an aqueous solution to the feedwater either just upstream or, preferably, just downstream of the deaerator, although it is sometimes added into the return lines to scavenge oxygen in the condensate.

The most widely used materials in this application are sodium sulfite ($Na_2SO_3$) and hydrazine ($N_2H_4$), both of which are usually sold as catalyzed systems to enhance reactivity with oxygen at lower temperatures and pressures. Quinones and cobalt salts are typically used as catalysts. Sulfite is the least expensive and most active (when catalyzed) for lower and medium pressure boilers [up to 600 psig (42 bar abs)]. In its reaction with oxygen, sodium sulfite produces sodium sulfate, which contributes solids to the circulating boiler system:

$$2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_4$$

Thus, in high pressure and supercritical boilers, where any solids constitute a severe problem, sulfite cannot be used.

The theoretical dosage of sodium sulfite, or the number of parts of $Na_2SO_3$ required to consume 1 part of $O_2$, can be calculated based on its reaction with oxygen described above:

$$\frac{2(126\ g/mole\ Na_2SO_3)}{32\ g/mole\ O_2} = 7.88\ theoretical$$

Therefore, about 8 parts of $Na_2SO_3$ are fed to the boiler to consume each part of oxygen. Typically, residual concentrations of sulfite of up to 25 - 60ppm are maintained in the boiler.

Sulfite also breaks down at pressures as low as 600 psig (41 bar abs) resulting in the formation of sulfur dioxide or hydrogen sulfide, by either of two routes:

$$Na_2SO_3 + H_2O \rightarrow SO_2 + 2\ NaOH$$
$$4\ Na_2SO_3 + 2\ H_2O \rightarrow H_2S + 2\ NaOH + 3\ Na_2SO_4$$

Both are corrosive gases, which leave the boiler with steam, resulting in low pH steam and condensate and potential attack throughout the system.

Sulfite is an effective oxygen scavenger, but it is nonvolatile and does not leave the boiler with the steam, thus providing no protection in the condensate system. Sulfite also does not reduce hematite to magnetite and is ineffective in repassivating boilers with existing rust.

The oxygen scavengers used in the higher pressure boilers, and the ones with which diethylhydroxylamine (DEHA) competes most directly are hydrazine and catalyzed hydrazine. Hydrazine does not produce corrosive gases at high temperatures and pressures, and in application, reacts with oxygen to form nitrogen and water:

$$N_2H_4 + O_2 \rightarrow 2\ H_2O + N_2$$

In calculating the theoretical requirement of hydrazine for scavenging oxygen, a value of 1 part per part oxygen is obtained:

$$\frac{32 \text{ g/mole hydrazine}}{32 \text{ g/mole } O_2} = 1$$

In operation, a 100% excess of hydrazine is used. Boiler residuals of 1ppm hydrazine are typically maintained.

Hydrazine does not contribute solids to the system, so boiler blowdown, or the mechanical removal of solids from the after-boiler section as sludge, is reduced. It also promotes the formation of the protective magnetite film on the boiler tubes and drum, and converts red iron dust (hematite) to magnetite. It is because of these passivation effects that an excess of scavenger to oxygen is required when changing a boiler system form a non-passivating scavenger to one, which passivates.

Hydrazine is not without limitations. It is not considered "volatile", so it does not leave the boiler with the steam to scavenge oxygen and passivate metal throughout the system. In boilers operating above 400°F (205°C), it can degrade to ammonia and volatilize with steam, and, in the presence of oxygen, attack metals containing copper:

$$2\ N_2H_4 \rightarrow 2\ NH_3 + N_2 + H_2$$

Finally, and most importantly of late, is the inclusion of hydrazine on the OSHA and NIOSH lists as a suspect carcinogen. Papers, sales literature presenting laboratory, and field data on "hydrazine alternatives" abound, and include those listed in Tables 1 and 2. Each claims to be a safe and effective material for boiler protection through oxygen scavenging, but the levels required and optimum conditions for use vary.

Carbohydrazide is a volatile oxygen scavenger, contributes no solids to the system, reacts readily with oxygen at low temperatures and pressures, and passivates the metal of the boiler system. Carbohydrazide can (and does) break down to hydrazine above temperatures of 350°F (180°C) to scavenge oxygen, but this conversion is not necessary for oxygen scavenging activity because it reacts directly with oxygen:

$$H_6N_4CO + 2O_2 \rightarrow CO_2 + 2N_2 + 3H_2O$$

The theoretical dosage required to scavenge one part $O_2$ is 1.4 parts carbohydrazide. It should be noted that in its reaction with oxygen, carbohydrazide creates carbon dioxide, a gas that when dissolved in the condensate as carbonic acid, $H_2CO_3$, results in corrosion in the return line. Carbohydrazide cannot be used in applications where the steam comes into contact with food.

Erythorbate, however, is generally regarded as safe (GRAS) by the FDA and can be used in food processing applications. It, too, is a metal passivator and contributes no solids to the system. It has a theoretical dosage level of 11 parts per oxygen (as $O_2$). Erythorbic acid is non-volatile. It will remain in the boiler, and will not travel with the stream to control oxygen corrosion in the condensate.

Methylethylketoxime, or MEKO, is a volatile oxygen scavenger, which displays metal passivating characteristics. It reacts with oxygen to form methyl ethyl ketone, nitrous oxide, and water:

$$2\ H_3C(C{=}N{-}OH)\ CH_2CH_3 + O_2 \rightarrow 2\ H_3C\ (C{=}O)\ CH_2\ CH_3 + N_2O + H_2O$$

Its theoretical dosage is 5.4 parts per part of oxygen.

Hydroquinone, which has been used to catalyze the reaction with $O_2$ of some of these oxygen scavengers, has been examined and proven to be effective itself in lowering $O_2$ levels to the 1-2 ppb range. It reacts with oxygen to form benzoquinone:

$$HOC_6H_4OH + 1/2O_2 \rightarrow H_2O + O = C_6H_4 = O$$

and has a theoretical dosage level of 6.9 parts per part O2. It is extremely reactive with oxygen at the lower boiler temperatures and pressures, and is volatile in higher pressure systems. It does not degrade to ammonia, so it is safe for use with copper-containin g alloys.

Diethylhydroxyla mine, or DEHA, is a volatile metal-passivati ng oxygen scavenger, which reacts with oxygen to form acetate, nitrogen and water:

$$4\ (CH_3CH_2)_2\ NOH + 9O_2 \rightarrow 8\ CH_3\ COOH + 2\ N_2 + 14\ H_20$$

In theory, 1.24 parts of DEHA react with 1 part of oxygen, but in application, a dosage of 3 : 1 DEHA to $O_2$ is recommended. It is generally true that all oxygen scavenger requirements in the field are larger (by up to a factor of 10) than projected by calculations.

DEHA has other advantages over each of the above-mentioned $O_2$ scavengers. It has higher volatility and metal passivating characteristics than sulfite, hydrazine and erythorbate, and can be used more safely than hydrazine. Less DEHA is required than erythorbate and methylethylketox ime in theoretical considerations. It offers toxicity advantages over carbohydroxide in that it does not yield hydrazine under use conditi ons. Relative to the other scavengers, catalyzed and uncatalyzed DEHA show excellent reactivity (e.g., rate of reaction) with oxygen. Catalyzed sodium sulfate is by far the most reactive oxygen scavenger available in the industry, which accounts for its use in low pressure systems. Among the preferred scavengers for higher pressure systems, DEHA has the highest rate of reaction with oxygen (Fig. 3 and 4). At 70 °F (21° C) and pH 8.5, DEHA lowers the level of dissolved oxygen from 9 to 4 ppm in 10 minutes, whereas with carbohydrazide, catalyzed hydrazine, and erythorbate, dissolved oxygen levels are still above 7 ppm. In thirty minutes, the $O_2$ levels for DEHA were below 1 ppm compared to levels near 6 ppm for the other scavengers. At pH 11, catalyzed DEHA compared favorably in rate of reaction with catalyzed sulfite. In both cases, the DEHA was catalyzed with hydroquinone.

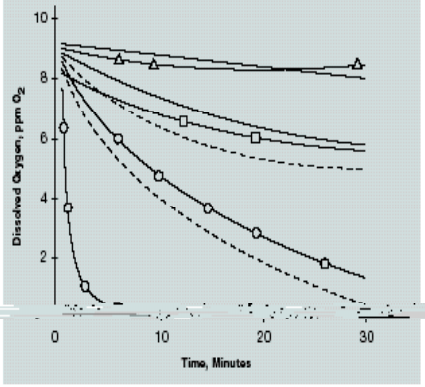
In considering thermal and oxidative degradati on products, DEHA generates dialkyl amines, acetaldehyde, acetaldoxime and acetic acid, the last of which can promote low pH corrosion in the system and add to boiler deposits as sodium or calc ium acetates. Several of the other scavengers, including erythorbate, MEKO, and hydroquinone also degrade into organic acids and negatively affect the boiler and after-boiler actions. As well, carbohydrazide produces $CO_2$ in its reaction with $O_2$, requiring additional prevention of corrosion due to low pH levels (as carbonic acid, $H_2CO_3$) in condensate return-lines.

For the most part, DEHA will find application as a replacement for hydrazine in medium and higher pressure boilers. In changing a steam-generati ng system from one to the other, a higher level of DEHA will be required at start-up to passivate the after-boiler and return-line sections of the system. After this has been accomplished, a 3 part DEHA per part oxygen dosage corresponds to a DEHA to hydrazine replacement ratio of 1.5.

(see following graphs)

NOTE: Please contact us or our nearest authorized distributors for more information relating to our ScaleGard ® Oxygen Scavengers.

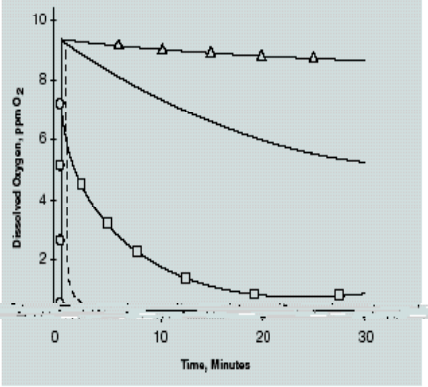
**Reaction Rates of Oxygen Scavengers at 70°F and pH 8.5**




The lower line for each product reflects the catalyzed version

- Carbohydrazide
- Hydrazine
- Erythorbic Acid
- DEHA
- Sulfite

**Reaction Rates of Oxygen Scavengers at 70°F and pH 11**




The Hydrazine, Sulfite, and DEHA used were catalyzed

- Carbohydrazide
- Hydrazine
- Erythorbic Acid
- DEHA
- Sulfite

**Table 1: Oxygen Scavengers**

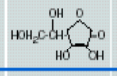
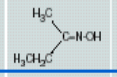
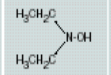
| Chemical Name | Structure | Product Name | Supplier |
|---|---|---|---|
| Carbohydrazide |  | Eliminox® | Nalco |
| Erythorbate |  | SulGard® | Nalco |
| Methylethylketoxime |  | Mekor® | Dearborn |
| Hydroquinone |  | Magni-Form® | Betz |
| Diethylhydroxylamine |  | Steamate® Neutrox® Conquor | Dearborn Calgon |

**Table 2: Oxygen Scavengers**

| Name | Volatily as VLDR | Metal Passivator | Contributes Solids | Toxicity | Theoretical Dosage (per part $O_2$) |
|---|---|---|---|---|---|
| Catalyzed Sulfite | non-volatile | N | Y | | 7.9 |
| Catalyzed Hydrazine | 0.08 | Y | N | suspect carcinogen | 1 |
| Carbohydrazide | volatile | Y | N | | 1.4 |
| Erythorbate | non volatile | Y | N | G.R.A.S. | 11 |
| Methylethyl-ketoxime | volatile | Y | N | | 5.4 |
| Hydroquinone | volatile | Y | N | | 6.9 |
| DEHA | 1.26 | Y | N | relatively non-toxic | 1.2 |

**TECHNICAL LITERATURE (2)**

***WHAT IS LEGIONNAIRES' DISEASE?***

Following the 1976 American Legion Convention at the Bellevue Stratford Hotel in Philadelphia, 34 attendees died and 221 people became ill from pneumonia of unknown cause apparently contracted while at the convention. This disease, now commonly known as the Legionnaires' disease, is caused by the bacterium *Legionella pneumophila.* The primary source of Legionella is from poorly controlled water systems. Legionnaires' Disease is becoming an issue in Southeast Asia. Singapore had introduced a legislation, and operators in Malaysia are becoming aware of the potential issues, with some already testing for the bacteria.

Legionnaires' Disease is a respiratory disease that strikes susceptible individuals exposed to *Legionella pneumophila.* Infection are caused by inhaling airborne water droplets or mists containing viable *Legionella pneumophila* which are small enough to pass deep into the lungs and to be deposited in the alveoli, the small pockets in the lungs.

The fatality rate is estimated at 10 to 12% of those who contract the disease; but in immuno-surppressed persons or those with other underlying diseases, this figure can be much higher.

The ecology of *Legionella pneumophila* in water system including the cooling tower is not fully understood. However, the following conditions have been found to affect its growth rate:

1. Sediment, sludge, scale, and organic materials can "harbor" the bacterium and promote growth. The formation of a biofilm within a water system is thought to play an important role in harboring and providing favorable conditions in which *Legionella pneumophila* can grow.
2. Water temperature in the range of 20°C to 45°C favor growth.
3. Stagnant water systems such as water basins, tanks, reservoirs, water fittings, piping, water heaters and upon some materials used in water systems.
4. Commonly encountered microorganisms in untreated or ineffectively treated water (such as algae, amoebae and other bacteria) may promote *Legionella pneumophila* growth.

Cooling towers are prone to colonization by *Legionella pneumophila* and have a potential for creating and disseminating aerosol droplets. Since *Legionella pneumophila* may be present in very low concentrations in the cooling tower systems, effective biological control is essential. Biocides can prevent the growth of *Legionella pneumophila* when properly applied

For more information on testing for the *Legionella pneumophila* in your water system, as well as our range of quality products that can effectively control this bacteria, please contact us or our nearest authorized distributors today.

Source: Cooling Tower Institute, Legionellosis Position Statement, WTP-148(96).

***Index 10***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** <ray.merrill@erg.com>
**Date:** Sun, Jan 7, 2007 2:16 PM
**Subject:** Hi Ray

Hi Ray

After a couple of months of inaction (with an operated Achilles tendon), I put my thoughts again on Method 202, this time on organic CPM.

My initial concerns were: and 1) is the methylene chloride extract residue weighed properly? 2) Would the organic CPM volatilize during the nitrogen purge?.

I did not know which compounds may become organic CPM. I started evaporation experiments with Naphthalene-Methylene chloride solutions, concluding that:

a) The residue of the methylene chloride extract evaporated at 3 mg/hr avg. following the evaporation of the methylene chloride at a 6650 mg/hr avg. The evaporation rate of the residue can be very roughly estimated by:

Evap.B = Evap.A * (VPB /VPA)* (MWB /MWA)

b) The 3 mg/hr evaporation rate would preclude reaching the constant weight criteria of Method 202 (<0.5 mg in 6 hr) until the evaporation of Naphthalene is complete.

Was it reasonable to expect a few mg of naphthalene in the methylene chloride extract of M 202?

To answer this question I made spreadsheets to model the distribution of organic compounds in the CTM-39 and M 202 trains. I got some low vapor pressure (0.0004 to 10 mmHg) data for hydrocarbons (alkanes C10-20, alkenes, polycyclic), including Antoine constants for that pressure range.

Based on these attached spreadsheets, I realized that naphthalene could not condense in M 202, unless the sample levels were >900 ppm methane

equivalent.

I was glad to confirm that CTM-039 and M 202 should theoretically produce similar organic CPM results, except for samples containing mid-range vapor pressure compounds (approximately 0.001 - 0.01 mm Hg @ 20 deg. C) for which the M 202 results would be higher than CTM-039. The discrepancy between the two methods depends on the hydrocarbon level of the samples, and the temperatures of the CTM-039 filter, and the M 202 condenser.

This coming week I plan to start additional evaporation runs with compounds of this critical mid-range vapor pressure, to verify that they are not lost while attempting to reach the constant weight criteria of Method 202. However, I think that Method 315 (section 11.2.4.1) have better guidance regarding CPM weighing.

Do you have any thoughts regarding my second initial concern (loss of CPM during N2 purge)?.

Regards

George Marson, P.Eng.

QA & EMS Supervisor

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**CC:** "Cianciarelli,Dominic [ETC]" <Dominic.Cianciarelli@ec.gc.ca>

**CONDENSABLE ORGANIC MATTER in CTM-039 and M 202 TRAINS**
**ALKANES**

| **Source Conditions** | | | | | | data entry | | results | | |
|---|---|---|---|---|---|---|---|---|---|---|
| HC as methane equiv., ppm | **20** | | | | | | | | | |
| Compound | n-Decane | n-Dodecane | n-Tridecane | n-Tetradecane | n-Pentadecane | n-Hexadecane | n-Heptadecane | n-Octadecane | n-Nonadecane | n-Eicosane |
| Carbon, n | 10 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Hydrogen, n | 22 | 26 | 28 | 30 | 32 | 34 | 36 | 38 | 40 | 42 |
| Boiling point, deg. C | 174 | 216 | 235 | 254 | 270 | 287 | 302 | 317 | 330 | 343 |
| A * | 8.5807 | 7.6682 | 7.7805 | 7.81799 | 8.4732 | 8.07352 | 6.9672 | 6.487 | 7.7142 | 8.8222 |
| B * | 2431.8 | 2023.9 | 2151.6 | 2236.75 | 2752.3 | 2522 | 1836 | 1582.4 | 2408 | 3272 |
| C * | 263.09 | 212.05 | 210.12 | 206.27 | 232.5 | 207.36 | 146.8 | 116.1 | 175 | 220 |
| | | | | | | | | | | |
| **CTM-039** | | | | | | | | | | |
| Sampling dilution factor | **20** | | | | | | | | | |
| Filter temperature, C | **10** | | | | | | | | | |
| Retained, % | 0 | | 0 | 0 | 0 | 0 | 59% | 98% | 88% | 90% |
| CPM, mg/m$^3$ | **0** | **0** | **0** | **0** | **0** | **0** | **8** | **13** | **11** | **12** |
| | | | | | | | | | | |
| **Method 202** | | | | | | | | | | |
| Filter temperature, C | **121** | | | | | | | | | |
| Retained in Filter, % | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Condenser temperature, C | **10** | | | | | | | | | |
| Potential condenser catch, % | | 0 | 0 | 0 | 0 | 69% | 98% | 100% | 99% | 99% |
| Total potential catch, % | 0% | 0% | 0% | 0% | 0% | 69% | 98% | 100% | 99% | 99% |
| CPM, mg/m$^3$ | **0** | **0** | **0** | **0** | **0** | **9** | **13** | **13** | **13** | **13** |
| Evaporation temperature, C | **20** | | | | | | | | | |
| VP @ cond. temp., mm Hg | 1/E-02 | 1/E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 |
| Est'd evaporation rate, mg/hr** | 95.8 | 10.4 | 3.4 | 1.2 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |

** Antoine parameters for 0.0004-10 mmHg range from Table 23-2(1.101)-kP page 2 of*
*TRCHP TABLES, Selected Values of Properties of Hydrocarbons and Related Compounds, API Research Project 44, June 1974, Texas A&M*
***based on 6650 mg/hr fumehood evaporation rate for methylene chloride (FW= 85, VP 350 mmHg @ 20 deg. C) in 5.7 cm. diam weighing pans*

**CONDENSABLE ORGANIC MATTER in CTM-039 and M 202 TRAINS**
**ALKENES**

| **Source Conditions** | | | | data entry | | results | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| HC as methane equiv., ppm | **20** | | | | | | | | | |
| Compound | n-Undecene | n-Dodecene | n-Tridecene | n-Tetradecene | n-Pentadecene | n-Hexadecene | n-Heptadecene | n-Octadecene | n-Nonadecene | n-Eicosene |
| Carbon, n | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Hydrogen, n | 22 | 24 | 26 | 28 | 30 | 32 | 34 | 36 | 38 | 40 |
| Boiling point, deg. C | 193 | 213 | 232 | 251 | 268 | 274 | 300 | 315 | 328 | 342 |
| A * | 6.96677 | 6.97607 | 9.4352 | 7.03065 | 8.764 | 8.6948 | 7.00867 | 6.5039 | 7.1151 | 7.1351 |
| B * | 1563.21 | 1621.11 | 3321.5 | 1754.09 | 2971.6 | 2976.6 | 1868.9 | 1594.5 | 1997.4 | 2043 |
| C * | 189.874 | 182.449 | 289.2 | 171.524 | 249.1 | 240.2 | 152.5 | 118.3 | 142.7 | 137.9 |
| | | | | | | | | | | |
| **CTM-039** | | | | | | | | | | |
| Sampling dilution factor | **20** | | | | | | | | | |
| Filter temperature, C | **10** | | | | | | | | | |
| Retained, % | | 0 | 0 | 0 | 0 | 0 | 28% | 97% | 97% | 99% |
| CPM, mg/m$^3$ | **0** | **0** | **0** | **0** | **0** | **0** | **4** | **13** | **13** | **13** |
| | | | | | | | | | | |
| **Method 202** | | | | | | | | | | |
| Filter temperature, C | **121** | | | | | | | | | |
| Retained in Filter, % | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Condenser temperature, C | **10** | | | | | | | | | |
| Potential condenser catch, % | | 0 | 0 | 0 | 0 | 34% | 96% | 100% | 100% | 100% |
| Total potential catch, % | 0% | 0% | 0% | 0% | 0% | 34% | 96% | 100% | 100% | 100% |
| CPM, mg/m$^3$ | **0** | **0** | **0** | **0** | **0** | **4** | **13** | **13** | **13** | **13** |
| Evaporation temperature, C | **20** | | | | | | | | | |
| VP @ cond. temp., mm Hg | 3.E-01 | 1/E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 |
| Est'd evaporation rate, mg/hr** | 5.7 | 3.5 | 2.0 | 0.3 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |

** Antoine parameters for 0.0004-10 mmHg range from Table 23-2(5.1101)-ka page 2, of*
*TRCHP TABLES, Selected Values of Properties of Hydrocarbons and Related Compounds, API Research Project 44, June 1974, Texas A&M*
***based on 6,650 mg/hr fumehood evaporation rate for methylene chloride (FW= 85, VP 350 mmHg @ 20 deg. C) in 5.7 cm. diam weighing pans*

**CONDENSABLE ORGANIC MATTER in CTM-039 and M 202 TRAINS**

**PAHs**

| **Source Conditions** | | | data entry | | results | | |
|---|---|---|---|---|---|---|---|
| THC, as ppm methane | **20** | | | | | | |
| Carbon, n | 10 | 14 | 14 | 18 | 18 | 18 | 18 |
| Hydrogen, n | 8 | 10 | 10 | 12 | 12 | 12 | 12 |
| Name | Naphtalene | Phenanthrene | Anthracene | Pyrene | Triphenylene | Benz(a)anthracene | Chrysene |
| Boiling point, deg. C | 218 | 336 | 340 | 404 | 429 | 438 | 448 |
| A * | 7.01065 | 9.631 | 9.21937 | 8.86349 | 12.89 | 13.68 | 13.07 |
| B * | 1733.71 | 4873.4 | 5152.94 | 5094.94 | 6154 | 6250 | 6340 |
| C * | 201.859 | 273.2 | 273 | 273.15 | 273 | 273 | 273.2 |
| | | | | | | | |
| **CTM-039** | | | | | | | |
| Sampling dilution factor | **20** | | | | | | |
| Filter temperature, C | **10** | | | | | | |
| Retained, % | | 100% | 100% | 100% | 100% | 100% | 100% |
| CPM, mg/m$^3$ | **0** | **13** | **13** | **13** | **13** | **13** | **13** |
| | | | | | | | |
| **Method 202** | | | | | | | |
| Filter temperature, C | **121** | | | | | | |
| Retained in Filter, % | | 0 | 87% | 90% | 0 | 0 | 0 |
| Condenser temperature, C | **10** | | | | | | |
| Potential condenser catch, % | | 100% | 13% | 10% | 100% | 100% | 100% |
| Total potential catch, % | 0% | 100% | 100% | 100% | 100% | 100% | 100% |
| CPM, mg/m$^3$ | **0** | **13** | **13** | **13** | **13** | **13** | **13** |
| Evaporation temperature, C | **20** | | | | | | |
| VP @ cond. temp., mm Hg | 2/E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 | 0.E-01 |
| Est'd evaporation rate, mg/hr** | 4.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

** Antoine parameters for 0.0004-10 mmHg range from Table 23-2(33.5810)-ka of*
*TRCHP TABLES, Selected Values of Properties of Hydrocarbons and Related Compounds, API Research Project 44, April 1975, Texas A&M*
***based on 6650 mg/hr fumehood evaporation rate for methylene chloride (FW= 85, VP 350 mmHg @ 20 deg. C) in 5.7 cm. diam weighing pans*

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca> ***Index 11***
**To:** <Myers.Ron@epamail.epa.gov>
**Date:** Thu, Jan 11, 2007 4:10 PM
**Subject:** FW: Meeting to discuss Improved Condensable PM test method.

Ooops... here are all the attachments.

-----Original Message-----
From: Marson, George (Jorge) [ETC]
Sent: Thursday, January 11, 2007 4:04 PM
To: 'Myers.Ron@epamail.epa.gov'
Subject: RE: Meeting to discuss Improved Condensable PM test method.

Hi Ron,

In the last few days I got to understand O-CPM a bit better. I put some thoughts in writing about this issue, which may interest some stakeholders. Certainly the conclusions are not surprising for experienced practitioners like Ray.

Hope that someone stakeholder will find a practical way to include condensable organic water soluble compounds into O-CPM.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

**CC:** "Cianciarelli,Dominic [ETC]" <Dominic.Cianciarelli@ec.gc.ca>, <ray.merrill@erg.com>

**ORGANIC CONDENSABLE PARTICULATE MATTER (O-CPM)**

During the ongoing review of Method 202 for testing emissions of condensable particulate matter from stationary sources, the following questions have been raised:

a) What organic compounds are likely to be captured as O-CPM in M 202?
b) Is the captured O-CPM likely to be lost during the M 202 nitrogen purge?
c) Should the constant weight I-CPM criterion apply to the weighing of O-CPM?
d) How does O-CPM and CTM 039 results may compare, for testing non-polar organic compounds?

### 1.1 Capture

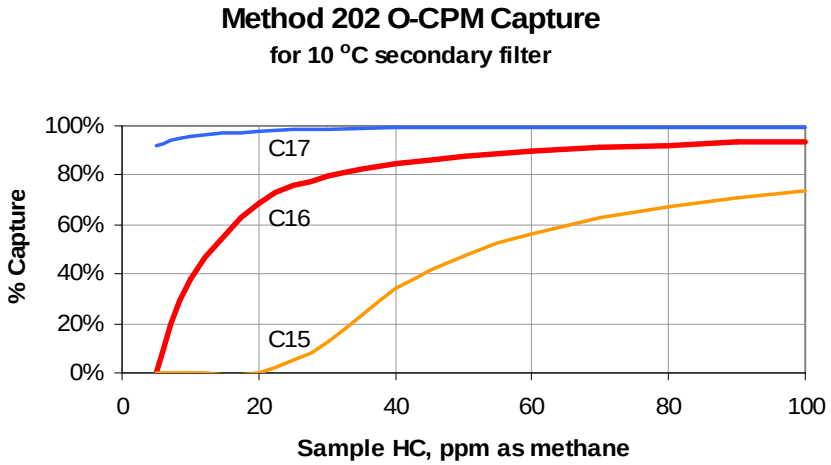
The capture of O-CPM in the M 202 train depends on various factors including compound vapor pressure, concentration, sample volume, and water solubility.

This theoretical discussion is based on the following typical conditions:

Sample containing a single n-alkenes compound
Hydrocarbon (HC) levels 0-100 ppm as methane
Sample and purge volume 1.2 $sm^3$

The fate of hydrocarbon vapors within the M 202 train was modeled on the basis of the vapor pressure of C10-C20 alkenes, estimated as a function of temperature from Antoine parameters applicable to the 0.004 to 10 mmHg range. The estimated capture of linear hydrocarbons as O-CPM is shown in Figure 1, as a function of concentration and carbon chain length.

**Figure 1**



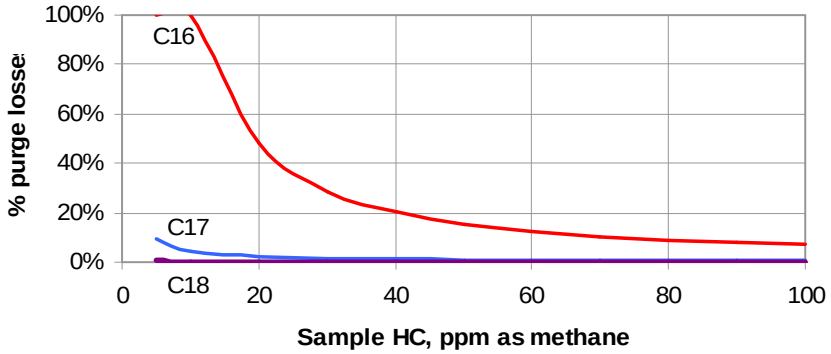

C17 and heavier hydrocarbons are fully retained by condensation. C15 and lighter are for the most part not retained. C16 (n-hexadecane, b.p. 287 °C, v.p. 0.0011 mmHg @ 21°C) represents an arbitrary boundary for O-CPM levels less than approximately 60 $mg/sm^3$.

### 1.2 Retention

The retention of the organic catch during the nitrogen purge depends on the volatility of the O-CPM, its temperature and quantity. The loss of linear hydrocarbons as result of the nitrogen purge is shown in Figure 2, as a function of concentration and carbon chain length.

Table 2

**Method 202 losses**
**for a 10°C purge**




Again C17 and heavier hydrocarbons are fully retained. C16 losses are significant at < 40 ppm as methane HC levels (23 mg/sm$^3$ O-CPM). Potential loss of lighter compounds is irrelevant, as these compounds are unlikely to be part of the catch.

### 1.3 Weighing

Following solvent extraction the residue of the methylene chloride (MC) must be determined gravimetrically. The MC solution is evaporated at ambient temperature and the residue weighted to constant weight (<0.5 mg change in 6 hours).

Following the evaporation of MC, the residue is exposed and it may also evaporate, albeit at much lower rate. The loss rate of semi volatile residue can be estimated from the vapor pressure (VP) and molecular weights (MS), with a relationship experimentally tested with Naphthalene-MC solutions.

$$\text{Loss rate}_{cx}\ (\text{mg/hr}) = \text{Loss rate}_{MC}\ (\text{mg/hr}) * (VP_{cx} / VP_{MC}) * (MW_{cx} / MW_{MC})$$

In laboratory fume hood conditions, MC evaporates from 5.7 cm aluminum drying pans at an average rate of 6650 mg/hr. The MC vapor pressure is approximately 400 mmHg. Therefore the loss rate of C16 is estimated as follows:

$$\text{Loss rate}_{c16}\ (\text{mg/hr}) = 6{,}650\ \text{mg/hr} * (0.0011\ \text{mmHg} / 400\ \text{mmHg}) * (226 / 97) = 0.04\ \text{mg/hr}$$
$$= 0.25\ \text{mg in 6 hours}$$

Since the loss rate is similar to the constant weight I-CPM criterion, it seems prudent to adopt the weighing procedure of Method 315 (residue desiccated for 1 hour after the evaporation of MC, followed by weighing).

### 1.4 Comparability

The net capture (capture and retention) of M 202 and CTM 039 for sampling hydrocarbon vapors was compared. The results are shown in Figures 3 and 4, respectively.

Figure 3

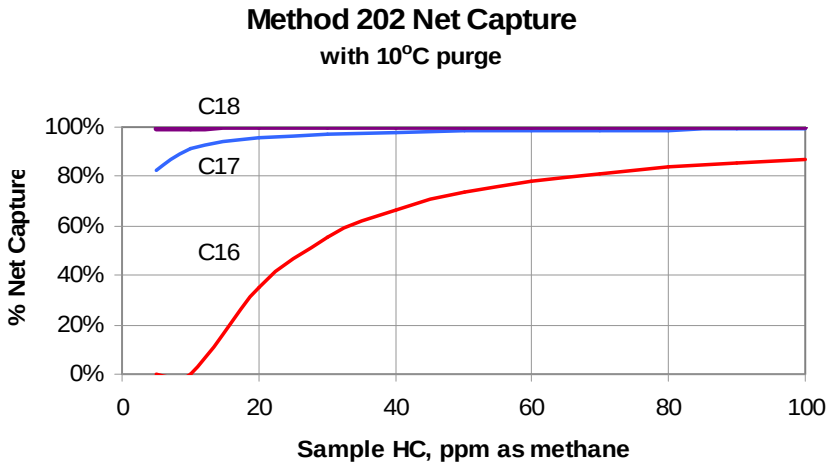
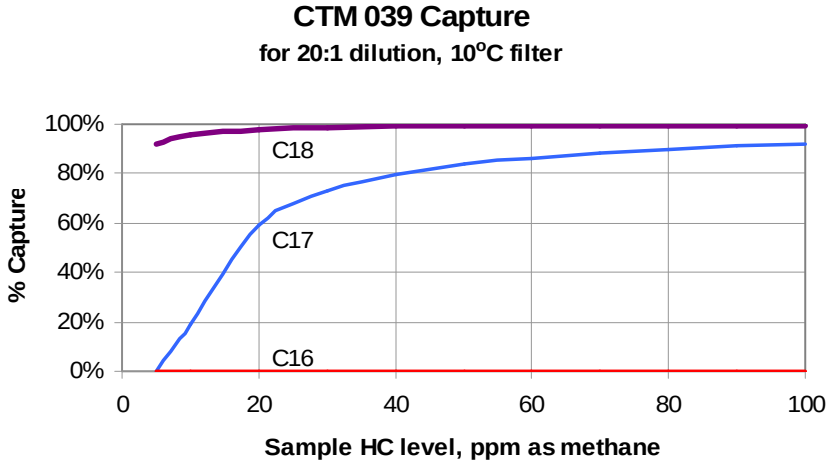



Figure 4




Method CTM 039 is unable to capture C16-like compounds, as result of the typical 20:1 sample dilution in which this method is based. Capture of C17 is significantly lower than M 202 at < 40 ppm as methane HC levels. Outside this narrow range of compounds, the O-CPM and CTM-039 results should be comparable.

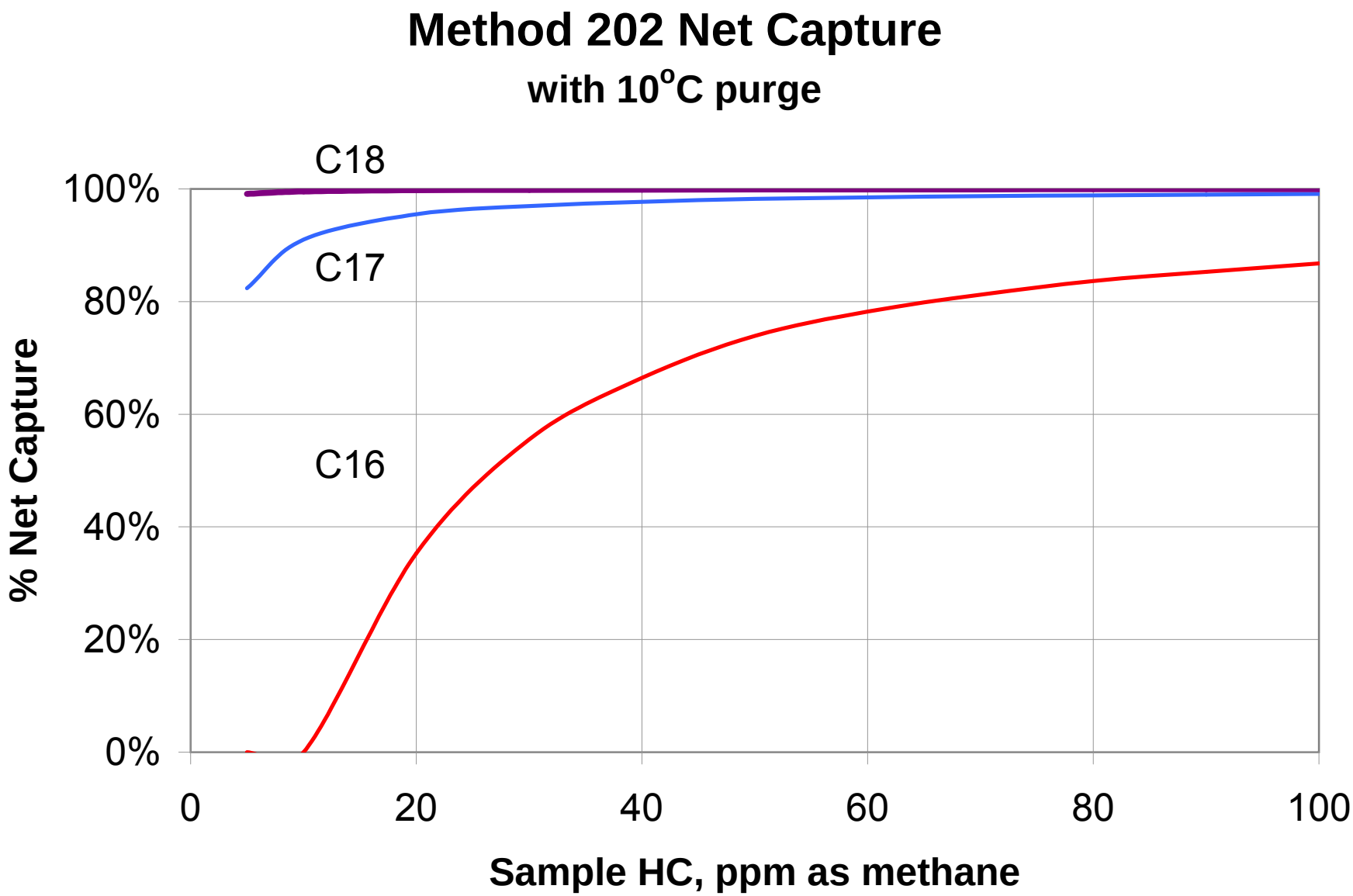
**DISTRIBUTION OF ORGANIC MATTER in M 202 TRAIN**

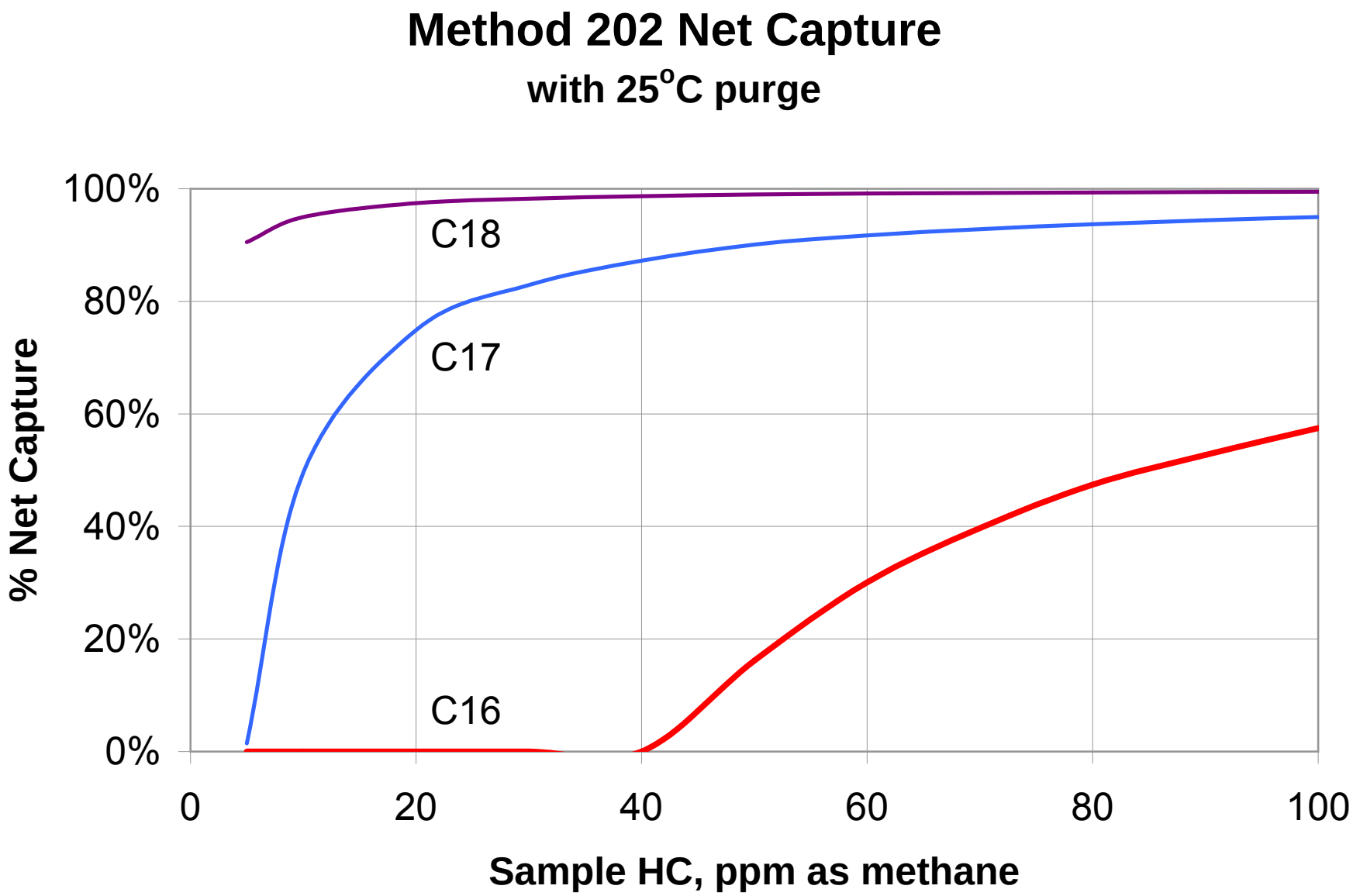
| | Stack Gas Sample Generator | | | |
|---|---|---|---|---|
| **Emission generator** | **1st Impinger** | **2nd Impinger** | | |
| Temperature, C | **28** | **35.2** | 50.3 | 62.5 |
| Compound | water | n-Hexadecane | n-Heptadecane | n-Octadecane |
| Oxygen, n | 1 | 0 | 0 | 0 |
| Carbon, n | 0 | 16 | 17 | 18 |
| Hydrogen, n | 2 | 34 | 36 | 38 |
| Boiling point, deg. C | 212 | 287 | 302 | 317 |
| A * | 8.08868 | 8.07352 | 6.9672 | 6.487 |
| B * | 1739.35100 | 2522 | 1836 | 1582.4 |
| C * | 234.10000 | 207.36 | 146.8 | 116.1 |
| Vapour pressure, mm Hg | 28.84380 | 0.00474 | 0.00449 | 0.00424 |
| Dry sample or purge volume, DSm3 | **1.20** | | | |
| Moisture, % v/v | 4% | 4% | 4% | 4% |
| HC as methane equiv., ppmw | | **100** | **100** | **100** |
| Evaporation (-) or condensation (+), mg | -34418 | -69 | -67 | -64 |
| Initial amount, mg | 500000 | 100000 | 100000 | 100000 |
| Balance, mg | 465582 | 99931 | 99933 | 99936 |
| Percent capture, % | | | | |
| N2 purge losses, % | | | | |
| Net Capture, % | | | | |

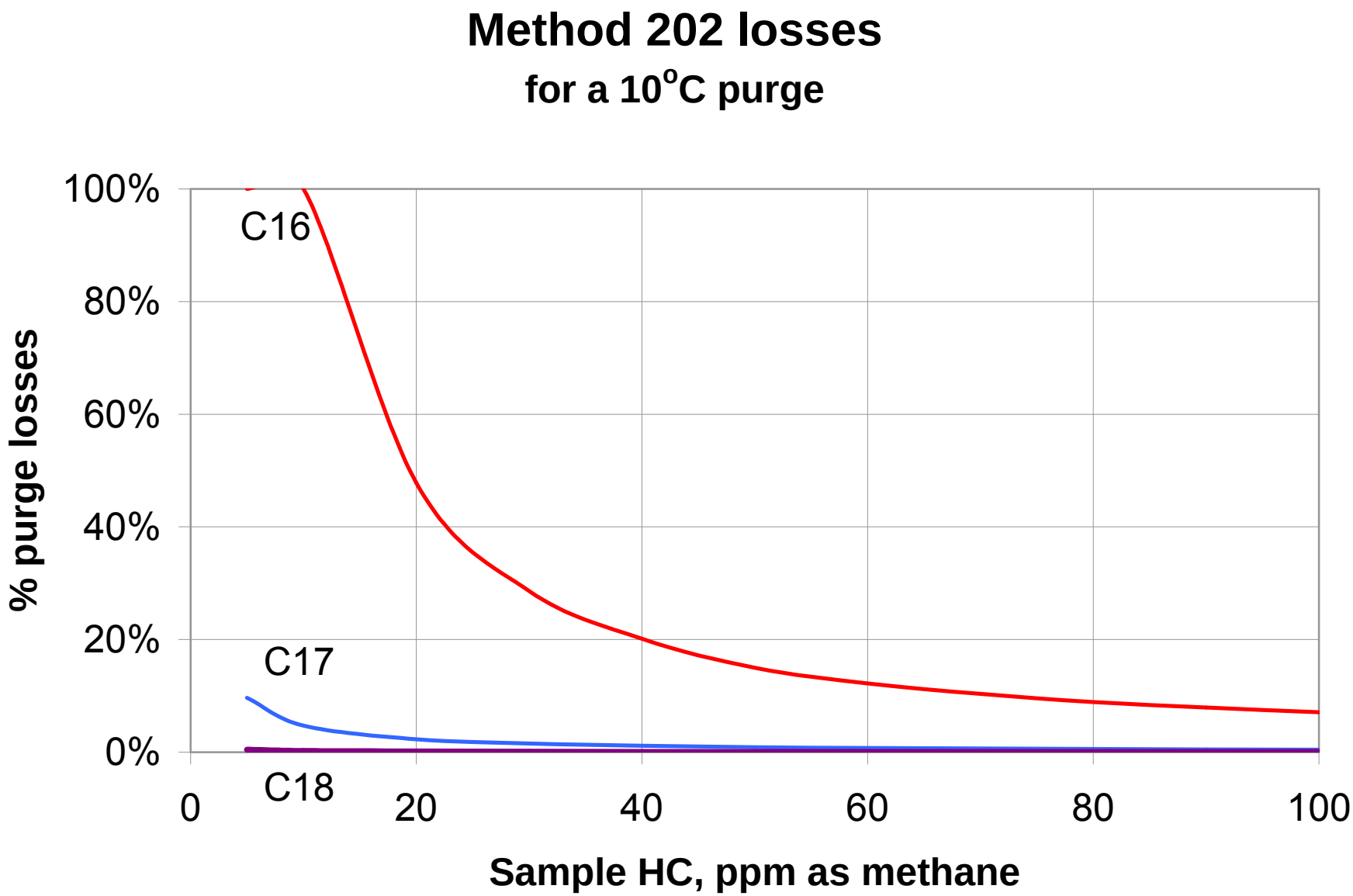
** Antoine parameters for 0.0004-10 mmHg range except for water which is for 30-60 mmHg range.*

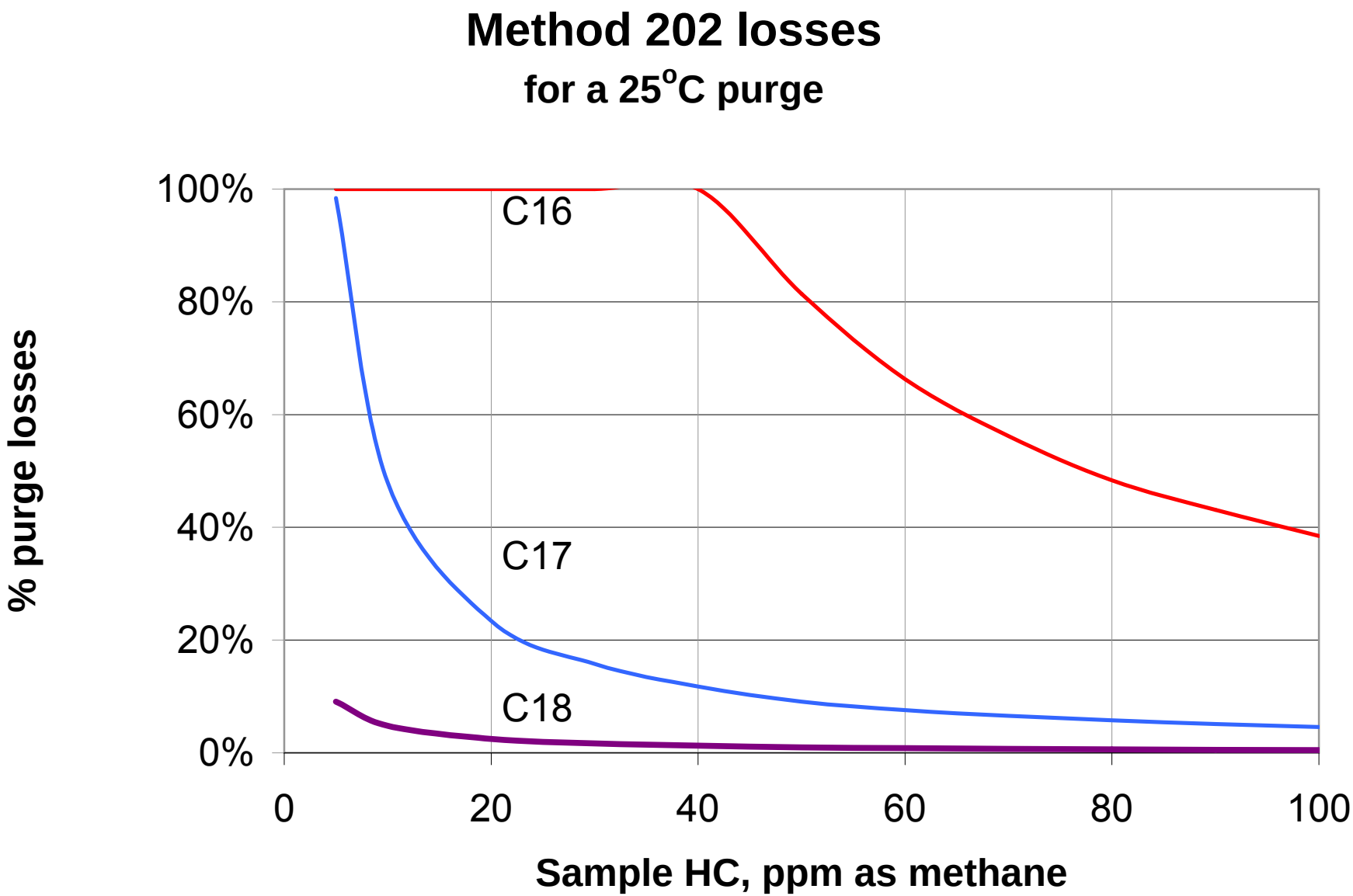
**Method 202 Train**

| Condenser + filter | | | | Nitrogen purge | | | |
|---|---|---|---|---|---|---|---|
| **10** | 10 | 10 | 10 | **25** | 25 | 25 | 25 |
| water | n-Hexadecane | n-Heptadecane | n-Octadecane | water | n-Hexadecane | n-Heptadecane | n-Octadecane |
| 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| 0 | 16 | 17 | 18 | 0 | 16 | 17 | 18 |
| 2 | 34 | 36 | 38 | 2 | 34 | 36 | 38 |
| 212 | 287 | 302 | 317 | 212 | 287 | 302 | 317 |
| 8.08868 | 8.07352 | 6.96720 | 6.48700 | 8.08868 | 8.07352 | 6.96720 | 6.48700 |
| 1739.35100 | 2522.00000 | 1836.00000 | 1582.40000 | 1739.35100 | 2522.00000 | 1836.00000 | 1582.40000 |
| 234.10000 | 207.36000 | 146.80000 | 116.10000 | 234.10000 | 207.36000 | 146.80000 | 116.10000 |
| 9.18564 | 0.00030 | 0.00002 | 0.00000 | 23.74804 | 0.00166 | 0.00019 | 0.00002 |
| | | | | | | | |
| 1.2% | 1.2% | 1.2% | 1.2% | 3.1% | 3.1% | 3.1% | 3.1% |
| | **6** | **0** | **0** | | **35** | **4** | **0** |
| -11379 | -5 | 0 | 0 | -28466 | -25 | -3 | 0 |
| 0 | 0 | 0 | 0 | 23039 | 65 | 66 | 64 |
| 23039 | 65 | 66 | 64 | 0 | 40 | 63 | 64 |
| | **93%** | **100%** | **100%** | | | | |
| | | | | | **38%** | **5%** | **0%** |
| | | | | | **57%** | **95%** | **99%** |


Method 202 Net Capture
with 10°C purge
C18
C17
C16
100%
80%
60%
40%
20%
0%
% Net Capture
0
20
40
60
80
100
Sample HC, ppm as methane


Method 202 Net Capture
with 25°C purge
% Net Capture
100%
80%
60%
40%
20%
0%
C18
C17
C16
0
20
40
60
80
100
Sample HC, ppm as methane


Method 202 losses
for a 10°C purge
100%
80%
60%
40%
20%
0%
% purge losses
C16
C17
C18
0
20
40
60
80
100
Sample HC, ppm as methane


Method 202 losses
for a 25°C purge
% purge losses
100%
80%
60%
40%
20%
0%
C16
C17
C18
0
20
40
60
80
100
Sample HC, ppm as methane

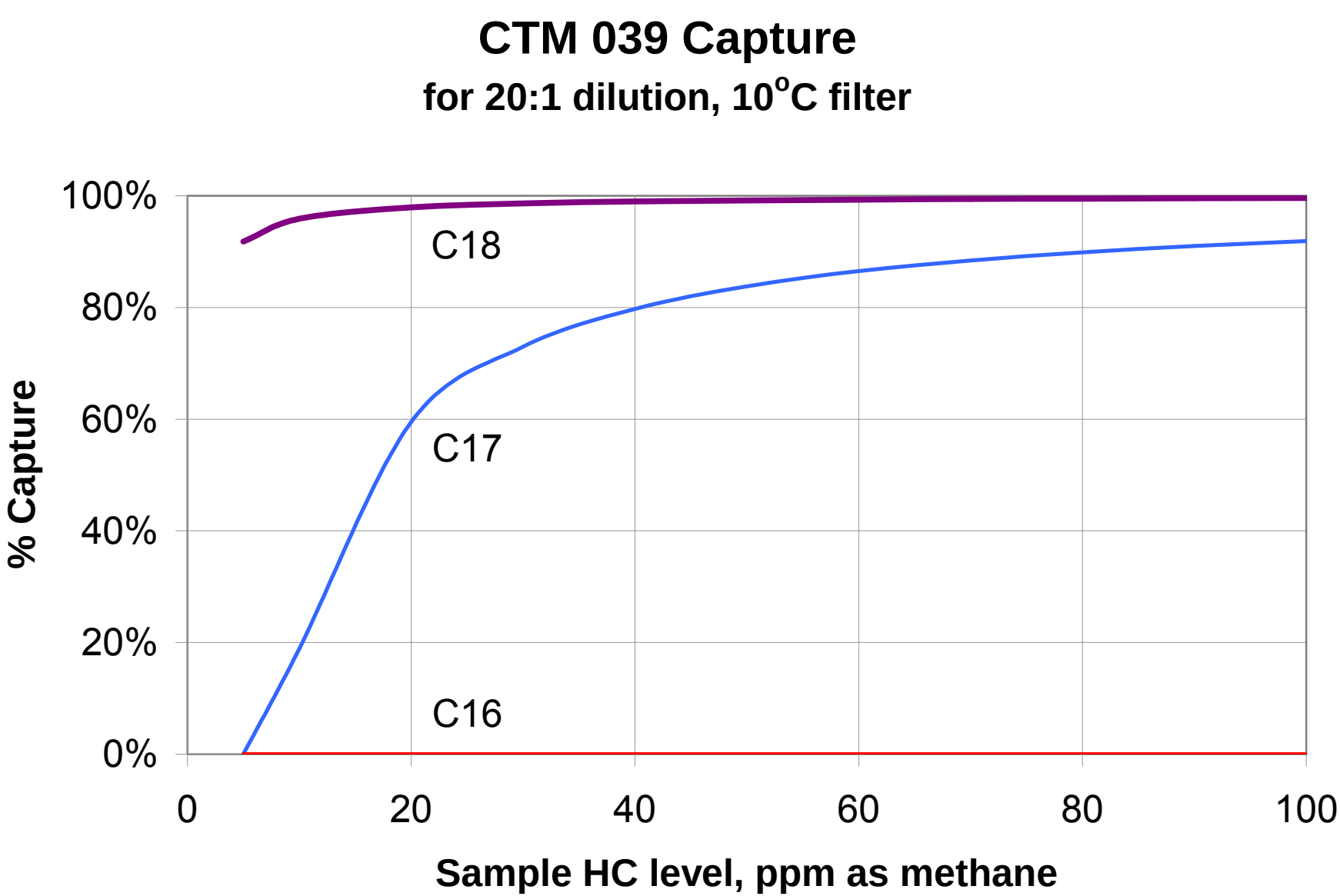
**CONDENSABLE ORGANIC MATTER in CTM-039 and M 202 TRAINS**

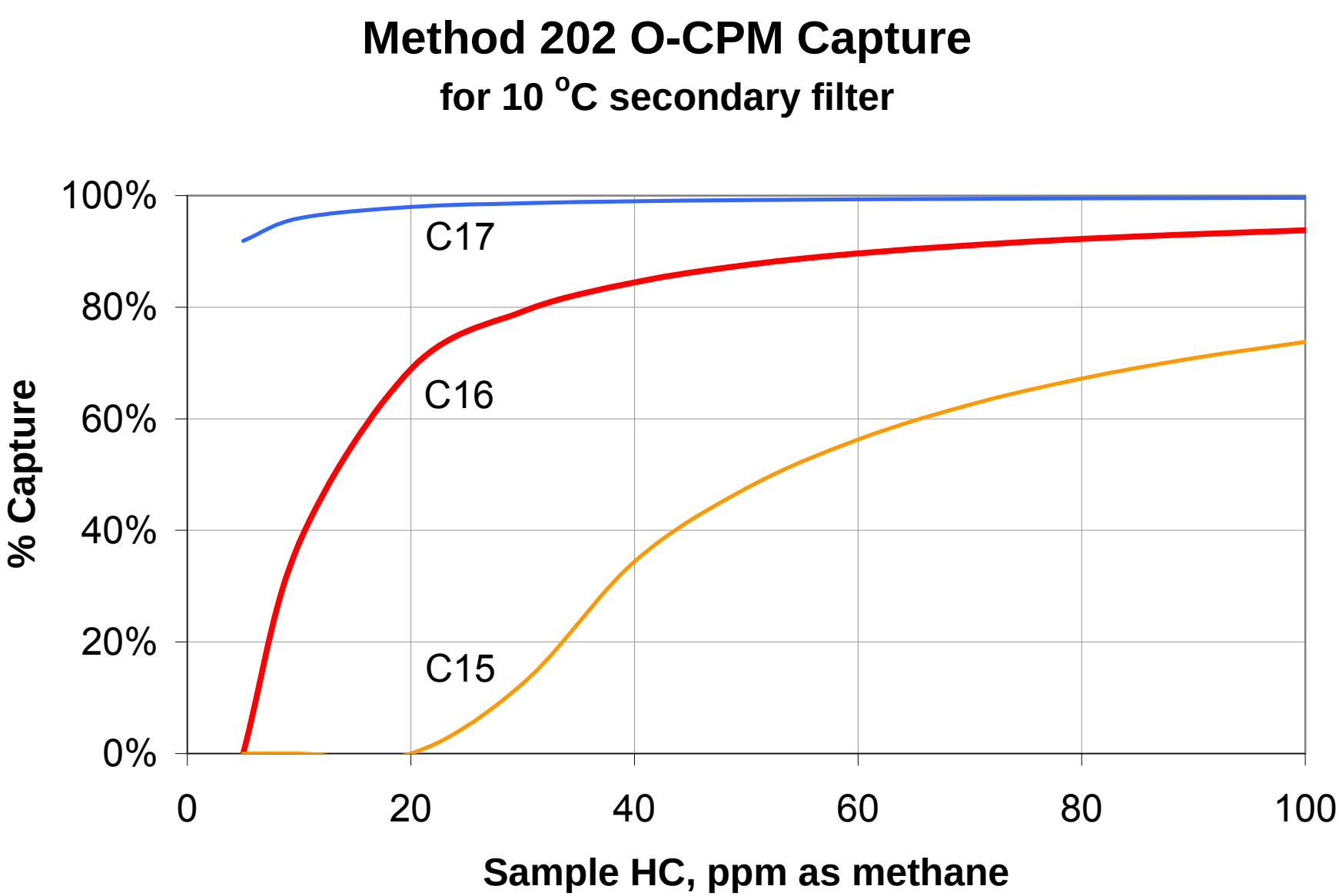
**ALKANES**

**Source Conditions** data entry

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| HC as methane equiv., ppm | **100** | | | | | | | | | |
| Compound | n-Decane | n-Dodecane | n-Tridecane | n-Tetradecane | n-Pentadecane | n-Hexadecane | n-Heptadecane | n-Octadecane | n-Nonadecane | n-Eicosane |
| Oxygen, n | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Carbon, n | 10 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Hydrogen, n | 22 | 26 | 28 | 30 | 32 | 34 | 36 | 38 | 40 | 42 |
| Boiling point, deg. C | 174 | 216 | 235 | 254 | 270 | 287 | 302 | 317 | 330 | 343 |
| A * | 8.5807 | 7.6682 | 7.7805 | 7.81799 | 8.4732 | 8.07352 | 6.9672 | 6.487 | 7.7142 | 8.8222 |
| B * | 2431.8 | 2023.9 | 2151.6 | 2236.75 | 2752.3 | 2522 | 1836 | 1582.4 | 2408 | 3272 |
| C * | 263.09 | 212.05 | 210.12 | 206.27 | 232.5 | 207.36 | 146.8 | 116.1 | 175 | 220 |
| VP corresponding to HC level, mmHG | 7.6E-03 | 6.3E-03 | 5.8E-03 | 5.4E-03 | 5.1E-03 | 4.8E-03 | 4.5E-03 | 4.2E-03 | 4.0E-03 | 3.8E-03 |
| | | | | | | | | | | |
| **CTM-039** | | | | | | | | | | |
| Sampling dilution factor | **20** | | | | | | | | | |
| Filter temperature, C | **10** | | | | | | | | | |
| VP @ filter temperature, mmHG | 4.7E-01 | 3.6E-02 | 1.0E-02 | 3.0E-03 | 1.3E-03 | 3.0E-04 | 1.8E-05 | 8.7E-07 | 5.0E-06 | 3.9E-06 |
| Retained, % | 0% | 0% | 0% | 0% | 0% | 0% | 92% | 100% | 98% | 98% |
| **CPM, mg/m3** | **0** | **0** | **0** | **0** | **0** | **0** | **54** | **58** | **57** | **57** |
| | | | | | | | | | | |
| **Method 202** | | | | | | | | | | |
| Sampling dilution factor | 1 | | | | | | | | | |
| Back up filter temperature, C | **10** | | | | | | | | | |
| VP @ filter temperature, mmHG | 4.7E-01 | 3.6E-02 | 1.0E-02 | 3.0E-03 | 1.3E-03 | 3.0E-04 | 1.8E-05 | 8.7E-07 | 5.0E-06 | 3.9E-06 |
| Retained, % | 0% | 0% | 0% | 45% | 74% | 94% | 100% | 100% | 100% | 100% |
| **CPM, mg/m3** | **0** | **0** | **0** | **26** | **43** | **55** | **58** | **58** | **58** | **58** |

** Antoine parameters for 0.0004-10 mmHg range from Table 23-2(1.101)-kP page 2 of*
*TRCHP TABLES, Selected Values of Properties of Hydrocarbons and Related Compounds, API Research Project 44, June 1974, Texas A&M*


CTM 039 Capture
for 20:1 dilution, 10°C filter
100%
80%
60%
40%
20%
0%
% Capture
C18
C17
C16
0
20
40
60
80
100
Sample HC level, ppm as methane


Method 202 O-CPM Capture
for 10 °C secondary filter
100%
80%
60%
40%
20%
0%
% Capture
C17
C16
C15
0
20
40
60
80
100
Sample HC, ppm as methane

***Index 12***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Thu, Feb 1, 2007 10:48 AM
**Subject:** CPM drying

Nice talking with you

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

**ORGANIC COMPOUNDS THAT PRODUCE CPM**

| | | | |
|---|---|---|---|
| **Stack gas CPM concentration, mg/Sm$^3$** | **20** | Data entry | Ultimate Results |
| **Sample volume, Sm$^3$** | **1.2** | | |
| **Reference temperature, $^o$C** | **20** | | |

| | Raw Data * | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Name | Formula | | | | | BP | FW | VP data, mmHg | | ** log (VP) | |
| | C | H | O | N | Other | | | 1 | 5 | 0 | 0.69897 |
| | n | n | n | n | | $^o$C | g/g-mol | $^o$C | $^o$C | 1 / $^o$K | 1 / $^o$K |
| Acetanilide | 8 | 9 | 1 | 1 | | 303.8 | 135.0 | 114.0 | 146.6 | 0.002584 | 0.002383 |
| Acridine | 13 | 9 | 0 | 1 | | 346.0 | 179.0 | 129.4 | 165.8 | 0.002485 | 0.002279 |
| Adipic acid | 6 | 10 | 4 | 0 | | 337.5 | 146.0 | 159.5 | 191.0 | 0.002312 | 0.002155 |
| 2-Anilinoethanol | 8 | 11 | 1 | 1 | | 279.6 | 137.0 | 104.0 | 134.3 | 0.002653 | 0.002455 |
| Anthracene | 14 | 10 | 0 | 0 | | 342.0 | 178.0 | 145.0 | 173.5 | 0.002392 | 0.00224 |
| Anthraquinone | 14 | 8 | 2 | 0 | | 379.9 | 208.0 | 190.0 | 219.4 | 0.00216 | 0.002031 |
| Azelaic acid | 9 | 16 | 4 | 0 | | 356.6 | 188.0 | 178.3 | 210.4 | 0.002216 | 0.002069 |
| Benzanthrone | 17 | 10 | 1 | 0 | | | 230.0 | 225.0 | 274.5 | 0.002008 | 0.001826 |
| Benzil | 14 | 10 | 2 | 0 | | 347.0 | 210.0 | 128.4 | 165.2 | 0.002491 | 0.002282 |
| Benzoic anhydride | 14 | 10 | 3 | 0 | | 360.0 | 226.0 | 143.8 | 180.0 | 0.002399 | 0.002208 |
| Benzoin | 14 | 12 | 2 | 0 | | 343.0 | 212.0 | 135.6 | 170.2 | 0.002447 | 0.002256 |
| Benzophenone | 13 | 10 | 1 | 0 | | 305.4 | 182.0 | 108.2 | 141.7 | 0.002623 | 0.002411 |
| Benzyl cinnamate | 16 | 14 | 2 | 0 | | 350.0 | 238.0 | 173.8 | 206.3 | 0.002238 | 0.002086 |
| 1-Biphenyloxy-2,3-epoxypropane | 15 | 14 | 2 | 0 | | 340.0 | 226.0 | 135.3 | 169.9 | 0.002449 | 0.002258 |
| Brassidic acid | 22 | 42 | 2 | 0 | | 382.5 | 338.0 | 209.6 | 241.7 | 0.002072 | 0.001943 |
| 3-Bromo-2,4,6-trichlorophenol | 6 | 2 | 1 | 0 | $BrCl_3$ | 305.8 | 276.4 | 112.4 | 146.2 | 0.002595 | 0.002385 |
| 1,2,3-Butanetriol | 4 | 10 | 3 | 0 | | 264.0 | 106.0 | 102.0 | 132.0 | 0.002667 | 0.002469 |
| iso-naphthylketone (1-isovaleronaphtone) | 15 | 16 | 1 | 0 | | 320.0 | 212.0 | 136.0 | 167.9 | 0.002445 | 0.002268 |
| 2-(4-tert-Butylphenoxy)ethyl acetate | 14 | 20 | 3 | 0 | | 304.4 | 236.0 | 118.0 | 150.0 | 0.002558 | 0.002364 |
| Capric acid | 10 | 20 | 2 | 0 | | 268.4 | 172.0 | 125.0 | 142.0 | 0.002513 | 0.00241 |
| 2-Chloro-3-phenylphenol | 12 | 9 | 1 | 0 | Cl | 317.5 | 204.5 | 118.0 | 152.2 | 0.002558 | 0.002352 |
| 2-Chloro-6-phenylphenol | 12 | 9 | 1 | 0 | Cl | 317.0 | 204.5 | 119.8 | 153.7 | 0.002546 | 0.002344 |
| trans-Cinnamic acid | 9 | 8 | 2 | 0 | | 300.0 | 148.0 | 127.5 | 157.8 | 0.002497 | 0.002321 |
| Coumarin | 9 | 6 | 2 | 0 | | 291.0 | 146.0 | 106.0 | 137.8 | 0.002639 | 0.002434 |
| 2-cyclohexyl-4,6-dinitrophenol | 12 | 14 | 5 | 2 | | 291.5 | 266.0 | 132.8 | 161.8 | 0.002464 | 0.0023 |
| Desoxybenzoin | 14 | 12 | 1 | 0 | | 321.0 | 196.0 | 123.3 | 156.2 | 0.002523 | 0.00233 |
| Dibenzylamine | 14 | 15 | 0 | 1 | | 300.0 | 197.0 | 118.3 | 149.8 | 0.002556 | 0.002365 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dibenzyl ketone (1,3-diphenyl-2-propanone) | 15 | 14 | 1 | 0 | | 330.5 | 210.0 | 125.5 | 159.8 | 0.002509 | 0.002311 |
| 4,6-Ditert-butyl-3-ethylphenol | 16 | 26 | 1 | 0 | | 290.0 | 234.0 | 111.5 | 142.6 | 0.002601 | 0.002406 |
| Dibutyl phtalate | 16 | 22 | 4 | 0 | | 340.0 | 278.0 | 148.2 | 182.1 | 0.002374 | 0.002197 |
| Diisobutyl d-tartrate | 12 | 22 | 6 | 0 | | 324.0 | 262.0 | 117.8 | 151.8 | 0.002559 | 0.002354 |
| Dicarvacryl-mono-(6-chloro-2-xenyl) phosphate | 32 | 34 | 4 | 0 | ClP | 361.0 | 548.4 | 204.2 | 234.5 | 0.002096 | 0.00197 |
| Dicarvacryl-2-tolyl phosphate | 27 | 33 | 4 | 0 | P | 330.0 | 452.0 | 180.2 | 209.3 | 0.002207 | 0.002073 |
| Dichlorodiphenyl silane | 12 | 10 | 0 | 0 | $Cl_2Si$ | 304.0 | 253.0 | 109.6 | 142.4 | 0.002614 | 0.002407 |
| Diethoxydiphenylsilane | 16 | 20 | 2 | 0 | Si | 296.0 | 272.0 | 111.5 | 142.8 | 0.002601 | 0.002405 |
| Diethyleneglycol-bis-chloroacetate | 8 | 12 | 5 | 0 | $Cl_2$ | 313.0 | 259.0 | 148.3 | 180.0 | 0.002374 | 0.002208 |
| Diethylhexadecylamine | 20 | 43 | 0 | 1 | | 355.0 | 297.0 | 139.8 | 175.8 | 0.002422 | 0.002228 |
| Diethyl phthalate | 12 | 14 | 4 | 0 | | 294.0 | 222.0 | 108.8 | 140.7 | 0.002619 | 0.002417 |
| Diethyl sebacate | 14 | 26 | 4 | 0 | | 305.5 | 258.0 | 125.3 | 156.2 | 0.002511 | 0.00233 |
| 1,4-Dihydroxyanthraquinone | 14 | 8 | 4 | 0 | | 450.0 | 240.0 | 196.7 | 239.8 | 0.002129 | 0.00195 |
| Diphenylamine | 12 | 11 | 0 | 1 | | 302.0 | 169.0 | 108.3 | 141.7 | 0.002623 | 0.002411 |
| Diphenyl chlorophosphate | 12 | 10 | 3 | 0 | ClP | 378.0 | 268.5 | 121.5 | 160.5 | 0.002535 | 0.002307 |
| Diphenyl disulphide | 12 | 10 | 0 | 0 | $S_2$ | 310.0 | 186.0 | 131.6 | 164.0 | 0.002472 | 0.002288 |
| trans-Diphenylethylene | 14 | 12 | 0 | 0 | | 306.5 | 180.0 | 113.2 | 145.8 | 0.002589 | 0.002388 |
| 1-1-Diphenylhydrazine | 12 | 12 | 0 | 2 | | 322.2 | 184.0 | 126.0 | 159.3 | 0.002506 | 0.002313 |
| Diphenyl-2-tolyl-thiophosphate | 18 | 17 | 3 | 0 | PS | 310.0 | 344.0 | 159.7 | 179.8 | 0.002311 | 0.002208 |
| Di-n-propyl d-tartrate | 10 | 18 | 6 | 0 | | 303.0 | 234.0 | 115.6 | 147.7 | 0.002573 | 0.002377 |
| Diisopropyl d-tartrate | 10 | 18 | 6 | 0 | | 275.0 | 234.0 | 103.7 | 133.7 | 0.002655 | 0.002459 |
| Docosane | 22 | 46 | 0 | 0 | | 376.0 | 310.0 | 157.8 | 195.4 | 0.002321 | 0.002135 |
| Elaidic acid | 18 | 34 | 2 | 0 | | 362.0 | 282.0 | 171.3 | 206.7 | 0.002251 | 0.002085 |
| Erucic acid | 22 | 42 | 2 | 0 | | 381.5 | 338.0 | 206.7 | 239.7 | 0.002085 | 0.00195 |
| Ethoxytriphenylsilane | 20 | 20 | 1 | 0 | Si | 344.0 | 304.0 | 167.0 | 198.2 | 0.002273 | 0.002122 |
| Ethyl benzoylacetate | 11 | 12 | 3 | 0 | | 265.0 | 192.0 | 107.6 | 136.4 | 0.002627 | 0.002443 |
| Ethylcamphoronic anhydride | 11 | 16 | 5 | 0 | | 298.0 | 228.0 | 118.2 | 149.8 | 0.002556 | 0.002365 |
| Ethyl carbanilate | 9 | 11 | 2 | 1 | | 237.0 | 165.0 | 107.8 | 131.8 | 0.002626 | 0.00247 |
| Ethylcetylamine | 18 | 39 | 0 | 1 | | 342.0 | 269.0 | 133.2 | 168.2 | 0.002462 | 0.002267 |
| Ethylene-bis-(chloroacetate) | 6 | 8 | 4 | 0 | $Cl_2$ | 283.5 | 215.0 | 112.0 | 142.4 | 0.002597 | 0.002407 |
| Ethyl α-naphtyl ketone (1-propionaphthone) | 13 | 12 | 1 | 0 | | 306.0 | 184.0 | 124.0 | 155.5 | 0.002519 | 0.002334 |
| Ethyl 3-nitrobenzoato | 9 | 9 | 4 | 1 | | 298.0 | 195.0 | 108.1 | 140.2 | 0.002624 | 0.00242 |
| Eugenyl acetate | 12 | 14 | 3 | 0 | | 282.0 | 206.0 | 101.6 | 132.3 | 0.00267 | 0.002467 |
| Fencholic acid | 10 | 16 | 2 | 0 | | 264.1 | 168.0 | 101.7 | 128.7 | 0.002669 | 0.002489 |
| Glutaric acid | 5 | 8 | 4 | 0 | | 303.0 | 132.0 | 155.5 | 183.8 | 0.002334 | 0.002189 |
| Glycerol | 3 | 8 | 3 | 0 | | 290.0 | 92.0 | 125.5 | 153.8 | 0.002509 | 0.002343 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Heneicosane | 21 | 44 | 0 | 0 | | 350.5 | 296.0 | 152.6 | 188.0 | 0.00235 | 0.002169 |
| Heptacosane | 27 | 56 | 0 | 0 | | 410.6 | 380.0 | 211.7 | 248.6 | 0.002063 | 0.001917 |
| Heptadecane | 17 | 36 | 0 | 0 | | 303.0 | 240.0 | 115.0 | 145.2 | 0.002577 | 0.002391 |
| Hexachlorobenzene | 6 | 0 | 0 | 0 | $Cl_6$ | 309.4 | 285.0 | 114.4 | 149.3 | 0.002581 | 0.002368 |
| Hexacosane | 26 | 54 | 0 | 0 | | 399.8 | 366.0 | 204.0 | 240.0 | 0.002096 | 0.001949 |
| Hexadecane | 16 | 34 | 0 | 0 | | 287.5 | 226.0 | 105.3 | 135.2 | 0.002643 | 0.00245 |
| 1-Hexadecene | 16 | 32 | 0 | 0 | | 274.0 | 224.0 | 101.6 | 131.7 | 0.00267 | 0.002471 |
| n-Hexadecyl alcohol (cetyl alcohol) | 16 | 34 | 1 | 0 | | 344.0 | 242.0 | 122.7 | 158.3 | 0.002527 | 0.002319 |
| n-Hexadecylamine (cetylamine) | 16 | 35 | 0 | 1 | | 330.0 | 241.0 | 123.6 | 157.8 | 0.002521 | 0.002321 |
| Hydroquinone | 6 | 6 | 2 | 0 | | 286.2 | 110.0 | 132.4 | 153.3 | 0.002467 | 0.002346 |
| 4-Hydroxybenzaldehyde | 7 | 6 | 2 | 0 | | 310.0 | 122.0 | 121.2 | 153.2 | 0.002537 | 0.002346 |
| Lauric acid | 12 | 24 | 2 | 0 | | 299.2 | 200.0 | 121.0 | 150.6 | 0.002538 | 0.002361 |
| Levulinic acid | 5 | 8 | 3 | 0 | | 245.8 | 116.0 | 102.0 | 128.1 | 0.002667 | 0.002493 |
| Mentyl benzoate | 17 | 24 | 2 | 0 | | 301.0 | 260.0 | 123.2 | 154.2 | 0.002524 | 0.002341 |
| α-Methylcinnamic acid | 10 | 10 | 2 | 0 | | 288.0 | 162.0 | 125.7 | 155.0 | 0.002508 | 0.002336 |
| N-Methyldiphenylamine | 13 | 13 | 0 | 1 | | 282.0 | 183.0 | 103.5 | 134.0 | 0.002656 | 0.002457 |
| 2-Methylheptadecane | 18 | 38 | 0 | 0 | | 306.5 | 254.0 | 119.8 | 152.0 | 0.002546 | 0.002353 |
| Methyl myristate | 15 | 30 | 2 | 0 | | 295.8 | 242.0 | 115.0 | 145.7 | 0.002577 | 0.002388 |
| Methyl α-naphthyl ketone (1-acetonaphtone) | 12 | 10 | 1 | 0 | | 295.5 | 170.0 | 115.6 | 146.3 | 0.002573 | 0.002385 |
| Methyl β-naphthyl ketone (2-acetonaphtone) | 12 | 10 | 1 | 0 | | 301.0 | 170.0 | 120.2 | 152.3 | 0.002543 | 0.002351 |
| Methyl palmitate | 17 | 34 | 2 | 0 | | | 270.0 | 134.3 | 166.8 | 0.002455 | 0.002274 |
| Methyl n-pentadecyl ketone (2-heptadecanone) | 17 | 34 | 1 | 0 | | 319.5 | 254.0 | 129.6 | 161.6 | 0.002484 | 0.002301 |
| Myristic acid (tetradecanoic acid) | 14 | 28 | 2 | 0 | | 318.0 | 228.0 | 142.0 | 174.1 | 0.00241 | 0.002237 |
| 1-Naphthoic acid | 11 | 8 | 2 | 0 | | 300.0 | 172.0 | 156.0 | 184.0 | 0.002331 | 0.002188 |
| 2-Naphthoic acid | 11 | 8 | 2 | 0 | | 308.5 | 172.0 | 160.8 | 189.7 | 0.002305 | 0.002161 |
| 3-Nitroaniline | 6 | 6 | 2 | 2 | | 305.7 | 138.0 | 119.3 | 151.5 | 0.002549 | 0.002356 |
| 4-Nitroaniline | 6 | 6 | 2 | 2 | | 336.0 | 138.0 | 142.4 | 177.6 | 0.002407 | 0.002219 |
| Nitroglycerine | 3 | 5 | 3 | 9 | | | 215.0 | 127.0 | 167.0 | 0.0025 | 0.002273 |
| 2-Nitrophenyl acetate | 8 | 7 | 4 | 1 | | 253.0 | 181.0 | 100.0 | 128.0 | 0.002681 | 0.002494 |
| Nonadecane | 19 | 40 | 0 | 0 | | 330.0 | 268.0 | 133.2 | 166.3 | 0.002462 | 0.002276 |
| Octadecane | 18 | 28 | 0 | 0 | | 317.0 | 244.0 | 119.6 | 152.1 | 0.002547 | 0.002352 |
| Oleic acid | 18 | 34 | 2 | 0 | | 360.0 | 282.0 | 176.5 | 208.5 | 0.002225 | 0.002077 |
| Palmitaldehyde | 16 | 32 | 1 | 0 | | 321.0 | 240.0 | 121.3 | 154.6 | 0.002536 | 0.002339 |
| Palmitic acid | 16 | 32 | 2 | 0 | | 353.8 | 256.0 | 153.6 | 188.1 | 0.002344 | 0.002169 |
| Palmitonitrile | 16 | 31 | 0 | 1 | | 332.0 | 237.0 | 134.3 | 168.3 | 0.002455 | 0.002266 |
| Pelargonic acid | 9 | 18 | 2 | 0 | | 253.5 | 158.0 | 108.2 | 126.0 | 0.002623 | 0.002506 |
| Pentacosane | 25 | 52 | 0 | 0 | | 390.3 | 352.0 | 194.2 | 230.0 | 0.00214 | 0.001988 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3,4 Pentanetriol | 5 | 12 | 3 | 0 | | 327.2 | 120.0 | 155.0 | 189.3 | 0.002336 | 0.002163 |
| Phenanthrene | 14 | 10 | 0 | 0 | | 340.2 | 178.0 | 118.2 | 154.3 | 0.002556 | 0.00234 |
| N-Phenyliminodiethanol | 10 | 15 | 2 | 1 | | 337.8 | 181.0 | 145.0 | 179.2 | 0.002392 | 0.002211 |
| Pimelic acid | 7 | 12 | 4 | 0 | | 342.1 | 160.0 | 163.4 | 196.2 | 0.002291 | 0.002131 |
| 4,4-iso-Propylidenebisphenol | 15 | 16 | 2 | 0 | | 360.5 | 228.0 | 193.0 | 224.2 | 0.002146 | 0.002011 |
| iso-Propyl β-naphthyl ketone (2-isobutyronaphthone) | 14 | 14 | 1 | 0 | | 313.0 | 198.0 | 133.2 | 165.4 | 0.002462 | 0.002281 |
| Resorcinol | 6 | 6 | 2 | 0 | | 276.5 | 110.0 | 108.4 | 138.0 | 0.002622 | 0.002433 |
| Salicylic acid | 7 | 6 | 3 | 0 | | 256.0 | 138.0 | 113.7 | 136.0 | 0.002586 | 0.002445 |
| Sebacic acid | 10 | 18 | 4 | 0 | | 352.3 | 202.0 | 183.0 | 215.7 | 0.002193 | 0.002046 |
| Steraldehyde | 18 | 36 | 1 | 0 | | 342.5 | 268.0 | 140.0 | 174.6 | 0.002421 | 0.002234 |
| Stearic acid | 18 | 36 | 2 | 0 | | 370.0 | 284.0 | 173.7 | 209.0 | 0.002239 | 0.002075 |
| Stearyl alcohol (1-octodecanol) | 18 | 38 | 1 | 0 | | 349.5 | 270.0 | 150.3 | 185.6 | 0.002362 | 0.002181 |
| Suberic acid | 8 | 14 | 4 | 0 | | 345.5 | 174.0 | 172.8 | 205.5 | 0.002243 | 0.00209 |
| Succinimide | 4 | 5 | 2 | 1 | | 287.5 | 99.0 | 115.0 | 143.2 | 0.002577 | 0.002403 |
| Tetracosane | 24 | 50 | 0 | 0 | | 386.4 | 338.0 | 183.8 | 219.6 | 0.002189 | 0.00203 |
| Tetradecyltetramethylsilane | 17 | 38 | 0 | 0 | Si | 300.0 | 270.0 | 120.0 | 150.7 | 0.002545 | 0.00236 |
| Tetraethylene glycol | 8 | 18 | 5 | 0 | | 307.8 | 194.0 | 153.9 | 183.7 | 0.002342 | 0.00219 |
| Tetraethylene glycol chlorohydrin | 8 | 17 | 4 | 0 | Cl | 281.5 | 212.5 | 110.1 | 141.8 | 0.00261 | 0.002411 |
| Tetrapropylene glycol monoisopropyl ether | 15 | 32 | 5 | 0 | | 292.7 | 292.0 | 116.6 | 147.8 | 0.002567 | 0.002376 |
| Toluene 2,4-diamine | 7 | 10 | 0 | 2 | | 280.0 | 122.0 | 106.5 | 137.2 | 0.002635 | 0.002438 |
| 2,4,6 Trichloroaniline | 6 | 4 | 0 | 1 | $Cl_3$ | 262.0 | 161.0 | 134.0 | 157.8 | 0.002457 | 0.002321 |
| Tri-2-chlorophenilthiophosphate | 18 | 12 | 3 | 0 | $Cl_3PS$ | 341.3 | 445.5 | 188.2 | 217.2 | 0.002168 | 0.00204 |
| Tricosane | 23 | 48 | 0 | 0 | | 366.5 | 324.0 | 170.0 | 206.3 | 0.002257 | 0.002086 |
| Tridecanoic acid | 18 | 26 | 2 | 0 | | 299.0 | 274.0 | 137.8 | 166.3 | 0.002434 | 0.002276 |
| Triethyl citrate | 12 | 20 | 7 | 0 | | 294.0 | 276.0 | 107.0 | 138.7 | 0.002632 | 0.002429 |
| Triethyleneglycol | 6 | 14 | 4 | 0 | | 278.3 | 150.0 | 114.0 | 144.0 | 0.002584 | 0.002398 |
| Triphenylmethane | 19 | 16 | 0 | 0 | | 259.2 | 244.0 | 169.7 | 188.4 | 0.002259 | 0.002167 |
| Triphenylphosphate | 18 | 15 | 4 | 0 | P | 413.5 | 326.0 | 193.5 | 230.4 | 0.002144 | 0.001986 |
| Tripropyleneglycol monobutyl ether | 13 | 28 | 4 | 0 | | 269.5 | 248.0 | 101.5 | 131.6 | 0.00267 | 0.002472 |
| Tritolylphosphate | 21 | 21 | 4 | 0 | P | 313.0 | 368.0 | 154.6 | 184.2 | 0.002339 | 0.002187 |
| 10-Undecenoid acid | 11 | 20 | 2 | 0 | | 275.0 | 184.0 | 114.0 | 142.0 | 0.002584 | 0.00241 |
| Vanillin | 8 | 8 | 3 | 0 | | 285.0 | 152.0 | 107.0 | 138.4 | 0.002632 | 0.002431 |
| 2-Xenyl dichlorophosphate | 12 | 9 | 1 | 0 | $Cl_2P$ | 328.5 | 271.0 | 138.2 | 171.1 | 0.002432 | 0.002252 |
| | | | | Average | | 317.4 | 225.7 | 136.2 | 168.0 | | |
| | | | | + / - range | | 132.6 | 322.7 | 88.8 | 106.5 | | |
| | | | | Count | | 130 | 133 | 133 | 133 | | |

** Selected vapour pressure data from Perry, Chemical Engineer's Handbook, 5th. Edition*

*** Low pressure values extrapolated as per Classius-Clapeyron equation [linear log(p) vs 1/T plots]*

| | | | | | Aqueous Fraction Drying | | | MC Fraction Drying | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Capture Conditions | | | | | Hours to dry 20 ml | | 20 | Hours to dry 20 ml | | 3 |
| 1 / °K | Temp. °C | | ***Catch | | 1 / °K | °C | ****Hours | 1 / °K | °C | ****Hours |
| 0.003534 | 10 | | | | 0.003195 | 40 | to lose | 0.00339 | 22 | to lose |
| log (VP) | mmHg | mg/Sm$^3$ | mg | % | log (VP) | mmHg | catch | log (VP) | mmHg | catch |
| -3.306156 | 4.9E-04 | 3.7E+00 | 19.6 | 82% | -2.126982 | 7.5E-03 | 20 | -2.805706 | 1.6E-03 | 95 |
| -3.555017 | 2.8E-04 | 2.7E+00 | 20.7 | 86% | -2.406672 | 3.9E-03 | 30 | -3.067652 | 8.6E-04 | 138 |
| -5.439021 | 3.6E-06 | 2.9E-02 | 24.0 | 100% | -3.930878 | 1.2E-04 | 1427 | -4.798955 | 1.6E-05 | 10535 |
| -3.120842 | 7.6E-04 | 5.7E+00 | 17.2 | 72% | -1.921171 | 1.2E-02 | 11 | -2.611693 | 2.4E-03 | 52 |
| -5.223751 | 6.0E-06 | 5.8E-02 | 23.9 | 100% | -3.673501 | 2.1E-04 | 646 | -4.565814 | 2.7E-05 | 5044 |
| -7.445868 | 3.6E-08 | 4.1E-04 | 24.0 | 100% | -5.610172 | 2.5E-06 | 47946 | -6.666786 | 2.2E-07 | 546218 |
| -6.259762 | 5.5E-07 | 5.7E-03 | 24.0 | 100% | -4.650911 | 2.2E-05 | 5825 | -5.576955 | 2.6E-06 | 49128 |
| -5.873399 | 1.3E-06 | 1.7E-02 | 24.0 | 100% | -4.56946 | 2.7E-05 | 3945 | -5.319998 | 4.8E-06 | 22210 |
| -3.482157 | 3.3E-04 | 3.8E+00 | 19.5 | 81% | -2.350667 | 4.5E-03 | 21 | -3.001945 | 1.0E-03 | 95 |
| -4.135403 | 7.3E-05 | 9.1E-01 | 22.9 | 95% | -2.900689 | 1.3E-03 | 82 | -3.611382 | 2.4E-04 | 422 |
| -3.973611 | 1.1E-04 | 1.2E+00 | 22.5 | 94% | -2.734612 | 1.8E-03 | 59 | -3.447772 | 3.6E-04 | 304 |
| -3.00243 | 9.9E-04 | 9.9E+00 | 12.1 | 50% | -1.885332 | 1.3E-02 | 5 | -2.528326 | 3.0E-03 | 23 |
| -5.966368 | 1.1E-06 | 1.4E-02 | 24.0 | 100% | -4.406506 | 3.9E-05 | 2620 | -5.304352 | 5.0E-06 | 20707 |
| -3.961437 | 1.1E-04 | 1.4E+00 | 22.4 | 93% | -2.724186 | 1.9E-03 | 53 | -3.436339 | 3.7E-04 | 276 |
| -7.904634 | 1.2E-08 | 2.3E-04 | 24.0 | 100% | -6.072803 | 8.5E-07 | 85612 | -7.127193 | 7.5E-08 | 970338 |
| -3.136726 | 7.3E-04 | 1.1E+01 | 10.7 | 45% | -2.005198 | 9.9E-03 | 4 | -2.656498 | 2.2E-03 | 18 |
| -3.067564 | 8.6E-04 | 5.0E+00 | 18.0 | 75% | -1.869131 | 1.4E-02 | 13 | -2.558941 | 2.8E-03 | 63 |
| -4.301224 | 5.0E-05 | 5.8E-01 | 23.3 | 97% | -2.963022 | 1.1E-03 | 103 | -3.733282 | 1.8E-04 | 606 |
| -3.526032 | 3.0E-04 | 3.8E+00 | 19.4 | 81% | -2.302498 | 5.0E-03 | 17 | -3.006756 | 9.8E-04 | 85 |
| -6.933765 | 1.2E-07 | 1.1E-03 | 24.0 | 100% | -4.633747 | 2.3E-05 | 6121 | -5.957622 | 1.1E-06 | 129039 |
| -3.31637 | 4.8E-04 | 5.4E+00 | 17.5 | 73% | -2.165589 | 6.8E-03 | 13 | -2.827971 | 1.5E-03 | 59 |
| -3.41348 | 3.9E-04 | 4.3E+00 | 18.8 | 78% | -2.243056 | 5.7E-03 | 16 | -2.916744 | 1.2E-03 | 77 |
| -4.126131 | 7.5E-05 | 6.1E-01 | 23.3 | 97% | -2.778148 | 1.7E-03 | 96 | -3.554038 | 2.8E-04 | 574 |
| -3.062998 | 8.6E-04 | 6.9E+00 | 15.7 | 65% | -1.903976 | 1.2E-02 | 9 | -2.571101 | 2.7E-03 | 41 |
| -4.547388 | 2.8E-05 | 4.1E-01 | 23.5 | 98% | -3.107089 | 7.8E-04 | 115 | -3.936115 | 1.2E-04 | 778 |
| -3.650613 | 2.2E-04 | 2.4E+00 | 21.1 | 88% | -2.426739 | 3.7E-03 | 29 | -3.131193 | 7.4E-04 | 149 |
| -3.590252 | 2.6E-04 | 2.8E+00 | 20.7 | 86% | -2.346931 | 4.5E-03 | 24 | -3.062579 | 8.7E-04 | 124 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| -3.599542 | 2.5E-04 | 2.9E+00 | 20.5 | 86% | -2.409203 | 3.9E-03 | 26 | -3.094354 | 8.0E-04 | 124 |
| -3.350065 | 4.5E-04 | 5.7E+00 | 17.1 | 71% | -2.13371 | 7.4E-03 | 10 | -2.833836 | 1.5E-03 | 51 |
| -4.58234 | 2.6E-05 | 4.0E-01 | 23.5 | 98% | -3.243759 | 5.7E-04 | 151 | -4.014237 | 9.7E-05 | 891 |
| -3.326568 | 4.7E-04 | 6.8E+00 | 15.9 | 66% | -2.170698 | 6.7E-03 | 9 | -2.836009 | 1.5E-03 | 42 |
| -8.033684 | 9.3E-09 | 2.8E-04 | 24.0 | 100% | -6.141589 | 7.2E-07 | 61821 | -7.230666 | 5.9E-08 | 758953 |
| -6.967162 | 1.1E-07 | 2.7E-03 | 24.0 | 100% | -5.189034 | 6.5E-06 | 8365 | -6.212512 | 6.1E-07 | 88302 |
| -3.115474 | 7.7E-04 | 1.1E+01 | 11.3 | 47% | -1.968412 | 1.1E-02 | 4 | -2.628653 | 2.4E-03 | 19 |
| -3.330261 | 4.7E-04 | 7.0E+00 | 15.6 | 65% | -2.121096 | 7.6E-03 | 8 | -2.817083 | 1.5E-03 | 38 |
| -4.881274 | 1.3E-05 | 1.9E-01 | 23.8 | 99% | -3.456063 | 3.5E-04 | 268 | -4.276405 | 5.3E-05 | 1769 |
| -3.996659 | 1.0E-04 | 1.6E+00 | 22.0 | 92% | -2.778402 | 1.7E-03 | 45 | -3.479623 | 3.3E-04 | 228 |
| -3.164637 | 6.8E-04 | 8.3E+00 | 14.0 | 58% | -1.992496 | 1.0E-02 | 6 | -2.667172 | 2.2E-03 | 30 |
| -3.955511 | 1.1E-04 | 1.6E+00 | 22.1 | 92% | -2.645845 | 2.3E-03 | 39 | -3.39968 | 4.0E-04 | 219 |
| -5.486396 | 3.3E-06 | 4.3E-02 | 23.9 | 100% | -4.163456 | 6.9E-05 | 1482 | -4.924931 | 1.2E-05 | 8559 |
| -3.014485 | 9.7E-04 | 8.9E+00 | 13.3 | 55% | -1.893749 | 1.3E-02 | 6 | -2.538837 | 2.9E-03 | 28 |
| -3.061057 | 8.7E-04 | 1.3E+01 | 8.7 | 36% | -2.023002 | 9.5E-03 | 3 | -2.6205 | 2.4E-03 | 14 |
| -4.050812 | 8.9E-05 | 9.1E-01 | 22.9 | 95% | -2.758964 | 1.7E-03 | 72 | -3.502543 | 3.1E-04 | 400 |
| -3.274469 | 5.3E-04 | 5.2E+00 | 17.7 | 74% | -2.099976 | 7.9E-03 | 13 | -2.776006 | 1.7E-03 | 60 |
| -3.719385 | 1.9E-04 | 1.9E+00 | 21.7 | 90% | -2.49318 | 3.2E-03 | 37 | -3.198975 | 6.3E-04 | 190 |
| -8.329219 | 4.7E-09 | 8.8E-05 | 24.0 | 100% | -6.021694 | 9.5E-07 | 74780 | -7.34989 | 4.5E-08 | 1592142 |
| -3.418247 | 3.8E-04 | 4.9E+00 | 18.1 | 76% | -2.212603 | 6.1E-03 | 13 | -2.906564 | 1.2E-03 | 64 |
| -3.137362 | 7.3E-04 | 9.3E+00 | 12.8 | 53% | -1.928442 | 1.2E-02 | 5 | -2.624288 | 2.4E-03 | 23 |
| -4.54753 | 2.8E-05 | 4.8E-01 | 23.4 | 98% | -3.277091 | 5.3E-04 | 146 | -4.008347 | 9.8E-05 | 785 |
| -5.398498 | 4.0E-06 | 6.2E-02 | 23.9 | 100% | -3.973245 | 1.1E-04 | 813 | -4.793611 | 1.6E-05 | 5379 |
| -7.547895 | 2.8E-08 | 5.2E-04 | 24.0 | 100% | -5.783612 | 1.6E-06 | 43988 | -6.799121 | 1.6E-07 | 455875 |
| -5.856288 | 1.4E-06 | 2.3E-02 | 24.0 | 100% | -4.283203 | 5.2E-05 | 1543 | -5.18866 | 6.5E-06 | 12415 |
| -3.426709 | 3.7E-04 | 3.9E+00 | 19.3 | 80% | -2.145933 | 7.1E-03 | 14 | -2.883139 | 1.3E-03 | 78 |
| -3.575586 | 2.7E-04 | 3.3E+00 | 20.0 | 83% | -2.336516 | 4.6E-03 | 19 | -3.049717 | 8.9E-04 | 100 |
| -4.07418 | 8.4E-05 | 7.6E-01 | 23.1 | 96% | -2.553719 | 2.8E-03 | 51 | -3.428886 | 3.7E-04 | 383 |
| -3.83575 | 1.5E-04 | 2.1E+00 | 21.4 | 89% | -2.6236 | 2.4E-03 | 34 | -3.321305 | 4.8E-04 | 170 |
| -3.442431 | 3.6E-04 | 4.2E+00 | 18.9 | 79% | -2.197048 | 6.4E-03 | 14 | -2.913882 | 1.2E-03 | 74 |
| -3.830163 | 1.5E-04 | 1.5E+00 | 22.2 | 93% | -2.551724 | 2.8E-03 | 44 | -3.287585 | 5.2E-04 | 239 |
| -3.118864 | 7.6E-04 | 8.1E+00 | 14.3 | 59% | -1.957567 | 1.1E-02 | 7 | -2.626001 | 2.4E-03 | 32 |
| -2.986798 | 1.0E-03 | 1.2E+01 | 10.1 | 42% | -1.816072 | 1.5E-02 | 3 | -2.489934 | 3.2E-03 | 15 |
| -3.369609 | 4.3E-04 | 3.9E+00 | 19.3 | 80% | -2.049922 | 8.9E-03 | 13 | -2.809525 | 1.6E-03 | 76 |
| -5.800625 | 1.6E-06 | 1.1E-02 | 24.0 | 100% | -4.163282 | 6.9E-05 | 2698 | -5.105725 | 7.8E-06 | 23635 |
| -4.302215 | 5.0E-05 | 2.5E-01 | 23.7 | 99% | -2.879508 | 1.3E-03 | 199 | -3.698408 | 2.0E-04 | 1312 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| -4.586583 | 2.6E-05 | 4.2E-01 | 23.5 | 98% | -3.27454 | 5.3E-04 | 152 | -4.029743 | 9.3E-05 | 867 |
| -7.04189 | 9.1E-08 | 1.9E-03 | 24.0 | 100% | -5.419955 | 3.8E-06 | 16935 | -6.35353 | 4.4E-07 | 145331 |
| -3.591191 | 2.6E-04 | 3.4E+00 | 20.0 | 83% | -2.319277 | 4.8E-03 | 18 | -3.051382 | 8.9E-04 | 95 |
| -3.120098 | 7.6E-04 | 1.2E+01 | 9.8 | 41% | -2.010401 | 9.8E-03 | 4 | -2.649135 | 2.2E-03 | 16 |
| -6.827924 | 1.5E-07 | 3.0E-03 | 24.0 | 100% | -5.218827 | 6.0E-06 | 11065 | -6.145013 | 7.2E-07 | 93351 |
| -3.213415 | 6.1E-04 | 7.6E+00 | 14.9 | 62% | -1.990807 | 1.0E-02 | 7 | -2.694532 | 2.0E-03 | 33 |
| -3.041825 | 9.1E-04 | 1.1E+01 | 10.6 | 44% | -1.849531 | 1.4E-02 | 3 | -2.535808 | 2.9E-03 | 17 |
| -3.372294 | 4.2E-04 | 5.6E+00 | 17.3 | 72% | -2.237429 | 5.8E-03 | 13 | -2.89065 | 1.3E-03 | 57 |
| -3.534272 | 2.9E-04 | 3.9E+00 | 19.4 | 81% | -2.351636 | 4.5E-03 | 18 | -3.032353 | 9.3E-04 | 88 |
| -6.16627 | 6.8E-07 | 4.1E-03 | 24.0 | 100% | -4.20877 | 6.2E-05 | 3597 | -5.335494 | 4.6E-06 | 48158 |
| -3.657972 | 2.2E-04 | 1.5E+00 | 22.2 | 93% | -2.415092 | 3.8E-03 | 48 | -3.130485 | 7.4E-04 | 251 |
| -3.923371 | 1.2E-04 | 1.3E+00 | 22.4 | 93% | -2.588591 | 2.6E-03 | 44 | -3.356881 | 4.4E-04 | 260 |
| -3.491983 | 3.2E-04 | 2.0E+00 | 21.5 | 90% | -2.127737 | 7.5E-03 | 25 | -2.912988 | 1.2E-03 | 155 |
| -3.852903 | 1.4E-04 | 2.0E+00 | 21.6 | 90% | -2.560396 | 2.8E-03 | 31 | -3.304354 | 5.0E-04 | 171 |
| -4.17428 | 6.7E-05 | 5.9E-01 | 23.3 | 97% | -2.795575 | 1.6E-03 | 92 | -3.589149 | 2.6E-04 | 569 |
| -3.081614 | 8.3E-04 | 8.3E+00 | 14.0 | 59% | -1.892267 | 1.3E-02 | 6 | -2.576847 | 2.6E-03 | 30 |
| -3.579377 | 2.6E-04 | 3.7E+00 | 19.6 | 82% | -2.35207 | 4.4E-03 | 18 | -3.0585 | 8.7E-04 | 90 |
| -3.536926 | 2.9E-04 | 3.8E+00 | 19.4 | 81% | -2.284231 | 5.2E-03 | 16 | -3.005274 | 9.9E-04 | 83 |
| -3.562235 | 2.7E-04 | 2.5E+00 | 20.9 | 87% | -2.305805 | 4.9E-03 | 25 | -3.028997 | 9.4E-04 | 134 |
| -3.606152 | 2.5E-04 | 2.3E+00 | 21.2 | 88% | -2.372897 | 4.2E-03 | 30 | -3.08275 | 8.3E-04 | 154 |
| -4.154465 | 7.0E-05 | 1.0E+00 | 22.8 | 95% | -2.849691 | 1.4E-03 | 61 | -3.60071 | 2.5E-04 | 343 |
| -4.011835 | 9.7E-05 | 1.4E+00 | 22.4 | 93% | -2.717452 | 1.9E-03 | 47 | -3.46249 | 3.4E-04 | 261 |
| -4.540939 | 2.9E-05 | 3.6E-01 | 23.6 | 98% | -3.17259 | 6.7E-04 | 157 | -3.960203 | 1.1E-04 | 962 |
| -5.885497 | 1.3E-06 | 1.2E-02 | 24.0 | 100% | -4.227955 | 5.9E-05 | 2403 | -5.182025 | 6.6E-06 | 21621 |
| -5.963141 | 1.1E-06 | 1.0E-02 | 24.0 | 100% | -4.318996 | 4.8E-05 | 2964 | -5.265355 | 5.4E-06 | 26197 |
| -3.558886 | 2.8E-04 | 2.1E+00 | 21.5 | 90% | -2.334582 | 4.6E-03 | 34 | -3.039283 | 9.1E-04 | 174 |
| -4.18609 | 6.5E-05 | 4.9E-01 | 23.4 | 98% | -2.927269 | 1.2E-03 | 146 | -3.651838 | 2.2E-04 | 776 |
| -3.178708 | 6.6E-04 | 7.8E+00 | 14.6 | 61% | -2.137106 | 7.3E-03 | 10 | -2.736645 | 1.8E-03 | 38 |
| -3.183471 | 6.6E-04 | 6.5E+00 | 16.2 | 68% | -1.918898 | 1.2E-02 | 8 | -2.646778 | 2.3E-03 | 40 |
| -4.038462 | 9.2E-05 | 1.3E+00 | 22.4 | 93% | -2.762252 | 1.7E-03 | 49 | -3.49683 | 3.2E-04 | 267 |
| -3.54071 | 2.9E-04 | 3.8E+00 | 19.4 | 81% | -2.325065 | 4.7E-03 | 17 | -3.024782 | 9.4E-04 | 86 |
| -6.187749 | 6.5E-07 | 1.0E-02 | 24.0 | 100% | -4.586624 | 2.6E-05 | 3348 | -5.508221 | 3.1E-06 | 27952 |
| -3.529886 | 3.0E-04 | 3.9E+00 | 19.3 | 81% | -2.3313 | 4.7E-03 | 18 | -3.021198 | 9.5E-04 | 86 |
| -4.740264 | 1.8E-05 | 2.5E-01 | 23.7 | 99% | -3.390538 | 4.1E-04 | 232 | -4.167431 | 6.8E-05 | 1388 |
| -3.984724 | 1.0E-04 | 1.3E+00 | 22.4 | 93% | -2.73326 | 1.8E-03 | 52 | -3.453594 | 3.5E-04 | 274 |
| -5.436714 | 3.7E-06 | 3.2E-02 | 24.0 | 100% | -3.413905 | 3.9E-04 | 401 | -4.57822 | 2.6E-05 | 5855 |
| -6.392146 | 4.1E-07 | 7.8E-03 | 24.0 | 100% | -4.838197 | 1.5E-05 | 4788 | -5.732639 | 1.9E-06 | 37547 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| -4.826918 | 1.5E-05 | 9.8E-02 | 23.9 | 100% | -3.461321 | 3.5E-04 | 587 | -4.247349 | 5.7E-05 | 3587 |
| -3.163188 | 6.9E-04 | 6.7E+00 | 16.0 | 67% | -2.067029 | 8.6E-03 | 11 | -2.697971 | 2.0E-03 | 46 |
| -4.408698 | 3.9E-05 | 3.9E-01 | 23.5 | 98% | -3.10033 | 7.9E-04 | 167 | -3.853418 | 1.4E-04 | 946 |
| -5.41978 | 3.8E-06 | 3.3E-02 | 24.0 | 100% | -3.941972 | 1.1E-04 | 1336 | -4.792588 | 1.6E-05 | 9471 |
| -7.202773 | 6.3E-08 | 7.8E-04 | 24.0 | 100% | -5.444803 | 3.6E-06 | 29888 | -6.456678 | 3.5E-07 | 307170 |
| -4.142834 | 7.2E-05 | 7.8E-01 | 23.1 | 96% | -2.833641 | 1.5E-03 | 81 | -3.587203 | 2.6E-04 | 459 |
| -3.374561 | 4.2E-04 | 2.5E+00 | 21.0 | 87% | -2.120901 | 7.6E-03 | 26 | -2.842499 | 1.4E-03 | 135 |
| -4.697527 | 2.0E-05 | 1.5E-01 | 23.8 | 99% | -3.018562 | 9.6E-04 | 184 | -3.984963 | 1.0E-04 | 1700 |
| -6.385763 | 4.1E-07 | 4.5E-03 | 24.0 | 100% | -4.772488 | 1.7E-05 | 7173 | -5.701078 | 2.0E-06 | 60853 |
| -4.153646 | 7.0E-05 | 1.0E+00 | 22.8 | 95% | -2.888871 | 1.3E-03 | 67 | -3.616867 | 2.4E-04 | 358 |
| -5.520687 | 3.0E-06 | 4.7E-02 | 23.9 | 100% | -4.076786 | 8.4E-05 | 1026 | -4.907886 | 1.2E-05 | 6953 |
| -4.50183 | 3.1E-05 | 4.7E-01 | 23.4 | 98% | -3.199993 | 6.3E-04 | 140 | -3.949322 | 1.1E-04 | 788 |
| -5.883838 | 1.3E-06 | 1.2E-02 | 24.0 | 100% | -4.339568 | 4.6E-05 | 3072 | -5.228439 | 5.9E-06 | 23783 |
| -3.827493 | 1.5E-04 | 8.1E-01 | 23.0 | 96% | -2.471886 | 3.4E-03 | 70 | -3.252164 | 5.6E-04 | 424 |
| -5.906541 | 1.2E-06 | 2.3E-02 | 24.0 | 100% | -4.418598 | 3.8E-05 | 1896 | -5.275048 | 5.3E-06 | 13623 |
| -3.749599 | 1.8E-04 | 2.6E+00 | 20.8 | 87% | -2.465609 | 3.4E-03 | 23 | -3.204665 | 6.2E-04 | 126 |
| -5.446878 | 3.6E-06 | 3.8E-02 | 24.0 | 100% | -3.898097 | 1.3E-04 | 996 | -4.789565 | 1.6E-05 | 7755 |
| -3.235085 | 5.8E-04 | 6.8E+00 | 15.9 | 66% | -2.048386 | 8.9E-03 | 9 | -2.731442 | 1.9E-03 | 41 |
| -3.550998 | 2.8E-04 | 4.5E+00 | 18.6 | 78% | -2.307088 | 4.9E-03 | 13 | -3.023074 | 9.5E-04 | 69 |
| -3.184613 | 6.5E-04 | 4.4E+00 | 18.8 | 78% | -1.984235 | 1.0E-02 | 15 | -2.675165 | 2.1E-03 | 74 |
| -5.543608 | 2.9E-06 | 2.5E-02 | 24.0 | 100% | -3.799625 | 1.6E-04 | 957 | -4.80345 | 1.6E-05 | 9654 |
| -7.439695 | 3.6E-08 | 8.9E-04 | 24.0 | 100% | -5.594196 | 2.5E-06 | 21577 | -6.656453 | 2.2E-07 | 249022 |
| -5.217866 | 6.1E-06 | 1.1E-01 | 23.9 | 99% | -3.833172 | 1.5E-04 | 512 | -4.630192 | 2.3E-05 | 3206 |
| -4.865408 | 1.4E-05 | 2.0E-01 | 23.8 | 99% | -3.366429 | 4.3E-04 | 206 | -4.229231 | 5.9E-05 | 1499 |
| -3.111469 | 7.7E-04 | 1.2E+01 | 10.0 | 42% | -1.943169 | 1.1E-02 | 3 | -2.615634 | 2.4E-03 | 15 |
| -3.570428 | 2.7E-04 | 2.2E+00 | 21.4 | 89% | -2.296999 | 5.0E-03 | 29 | -3.029976 | 9.3E-04 | 156 |
| -9.732244 | 1.9E-10 | 2.5E-06 | 24.0 | 100% | -7.146447 | 7.1E-08 | 1405107 | -8.634814 | 2.3E-09 | 43259033 |
| -6.18294 | 6.6E-07 | 1.2E-02 | 24.0 | 100% | -4.676376 | 2.1E-05 | 3561 | -5.543544 | 2.9E-06 | 26226 |
| -3.037754 | 9.2E-04 | 1.2E+01 | 9.1 | | -1.846072 | 1.4E-02 | 3 | -2.531996 | 2.9E-03 | 13 |
| -5.516389 | 3.0E-06 | 6.1E-02 | 23.9 | 100% | -3.952877 | 1.1E-04 | 595 | -4.852824 | 1.4E-05 | 4724 |
| -3.807111 | 1.6E-04 | 1.6E+00 | 22.1 | 92% | -2.449266 | 3.6E-03 | 34 | -3.230832 | 5.9E-04 | 209 |
| -3.138907 | 7.3E-04 | 6.0E+00 | 16.7 | 70% | -1.960305 | 1.1E-02 | 10 | -2.6387 | 2.3E-03 | 49 |
| -4.274103 | 5.3E-05 | 7.9E-01 | 23.1 | 96% | -2.960128 | 1.1E-03 | 79 | -3.716443 | 1.9E-04 | 451 |
| | 2.5E-04 | 2.8E+00 | | 86% | | 3.9E-03 | | | 8.0E-04 | |
| | 7.8E-04 | 1.0E+01 | | | | 1.1E-02 | | | 2.4E-03 | |
| | 133 | 133 | 133 | | | | | | | |

*** *Estimated capture for the specified CPM sample concentration*

**** *Estimated for a 5.7cm diam. drying pan*

| | | | | |
|---|---|---|---|---|
| Exp'l water loss rate at 10% RH a | **22** | °C = | **0.35** | g/hr |
| Water vapour pressure at | 22 | °C = | 19.83 | mmHg |
| Water vapour pressure at | 40 | °C = | 55.33 | mmHg |
| Est'd water loss rate at 10% RH a | **40** | °C = | **0.98** | g/hr |
| Time to evaporate last 20 ml of water | | | **20** | hours |
| | | | | |
| Experimental MC loss rate at | **22** | °C = | **7.86** | g/hr |
| Time to evaporate last 20 ml of MC | | | **3** | hours |

**INORGANIC COMPOUNDS THAT PRODUCE CPM**

| | | | |
|---|---|---|---|
| **Stack gas concentration, mg/Sm$^3$** | **20** | Data entry | Results |
| **Sample volume, Sm$^3$** | **1.2** | | |
| **Reference temperature, $^o$C** | **20** | | |

| | Raw Data * | | | | | | | Capture Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Name | Formula | FW | BP | MP | VP data, mmHg 1 | 5 | **log (VP) 0 | 0.69897 | 1 / $^o$K 0.003534 | Temp. $^o$C **10** | | ***C |
| | | g/g-mol | $^o$C | $^o$C | $^o$C | $^o$C | 1 / $^o$K | 1 / $^o$K | log (VP) | mmHg | mg/Sm$^3$ | mg |
| Aluminum bromide | $AlBr_3$ | 266.72 | 256.3 | 97.0 | 81.3 | 103.8 | 0.002822 | 0.002654 | -2.949103 | 1.1E-03 | 1.6E+01 | 4.3 |
| Aluminum chloride | $AlCl_3$ | 133.34 | 180.2 | 192.4 | 100 | 116.4 | 0.002681 | 0.002568 | -5.277968 | 5.3E-06 | 3.8E-02 | 24.0 |
| Ammonium chloride | $NH_4Cl$ | 53.5 | 337.8 | 520 | 160.4 | 193.8 | 0.002307 | 0.002142 | -5.191637 | 6.4E-06 | 1.9E-02 | 24.0 |
| Antimony triiodide | $SbI_3$ | 502.45 | 401 | 167 | 163.6 | 203.8 | 0.00229 | 0.002097 | -4.499596 | 3.2E-05 | 8.7E-01 | 23.0 |
| Mercury | Hg | 200.61 | 357 | -38.9 | 126.2 | 164.8 | 0.002505 | 0.002284 | -3.255118 | 5.6E-04 | 6.1E+00 | 16.7 |
| Mercury bromide | $HgBr_2$ | 360.44 | 319 | 237 | 136.5 | 165.3 | 0.002442 | 0.002282 | -4.754902 | 1.8E-05 | 3.5E-01 | 23.6 |
| Mercury chloride | $HgCl_2$ | 271.52 | 304 | 277 | 136.2 | 166 | 0.002444 | 0.002278 | -4.591766 | 2.6E-05 | 3.8E-01 | 23.5 |
| Mercury iodide | $HgI_2$ | 454.39 | 354 | 259 | 157.5 | 189.2 | 0.002323 | 0.002164 | -5.311715 | 4.9E-06 | 1.2E-01 | 23.9 |
| Selenium dioxide | $SeO_2$ | 110.96 | 317 | 340 | 157 | 187.7 | 0.002326 | 0.002171 | -5.448404 | 3.6E-06 | 2.2E-02 | 24.0 |

**Selected vapour pressure data from Perry, Chemical Engineer's Handbook, 5th. Edition*

***Low pressure values extrapolated as per Classius-Clapeyron equation [linear log(p) vs 1/T plots]*

**** Estimated capture for the specified CPM sample concentration*

| | Aqueous Fraction Drying | | |
|---|---|---|---|
| | Hours to dry 20 ml: | | **20** |
| atch | 1 / °K | °C | ****Hours |
| | 0.003195 | **40** | to lose |
| % | log (VP) | mmHg | catch |
| 18% | -1.544517 | 2.9E-02 | 1 |
| 100% | -3.181395 | 6.6E-04 | 278 |
| 100% | -3.757726 | 1.7E-04 | 2616 |
| 96% | -3.27373 | 5.3E-04 | 87 |
| 69% | -2.183282 | 6.6E-03 | 13 |
| 98% | -3.279597 | 5.3E-04 | 127 |
| 98% | -3.164736 | 6.8E-04 | 129 |
| 99% | -3.825804 | 1.5E-04 | 358 |
| 100% | -3.920847 | 1.2E-04 | 1836 |

**** *Estimated for a 5.7cm diam. drying pan*

| | | | | |
|---|---|---|---|---|
| Exp'l water loss rate at 10% RH a | **22** | °C = | **0.35** | g/hr |
| Water vapour pressure at | 22 | °C = | 19.83 | mmHg |
| Water vapour pressure at | 40 | °C = | 55.33 | mmHg |
| Est'd water loss rate at 10% RH a | **40** | °C = | **0.98** | g/hr |
| Time to evaporate last 20 ml of water | | | **20** | hours |

***Index 13***

**From:** "Steve Eckard" <steve.eckard@enthalpy.com>
**To:** <Myers.Ron@epamail.epa.gov>, <Ray.Merrill@erg.com>
**Date:** Fri, Feb 2, 2007 4:18 PM
**Subject:** RE: Feb 9 meeting to discuss improved condensable PM test method

Ray, Ron

I plan to attend most of the day. I have a lunch commitment with 25 of my employees for which I will leave and come back.

We did complete the 3 temperature tests for SO4= loss during evaporation that I mentioned to you. It got set aside in QA and I am told will be reviewed by early next week. I'll forward it to you as soon as I have it from QA.

Steve Eckard

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Wednesday, January 31, 2007 6:48 PM
To: PMUELLER@epri.com; gaburn@mde.state.md.us; Huntley.Roy@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Westlin.Peter@epamail.epa.gov; Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov; Oldham.Conniesue@epamail.epa.gov; marksh@kochind.com; Sorrell.Candace@epamail.epa.gov; ewstewart@mactec.com; glenn.england@ge.com; Garry Brooks; John Richards; mdmaret@mactec.com; shannon.vogel@ncmail.net; Driscoll.Tom@epamail.epa.gov; ngoodman@epri.com; Dominic Cianciarelli; hschiff@trcsolutions.com; Joe Fanjoy; Hardin.Erik@epamail.epa.gov; seebea@dnr.state.wi.us; mstewartdouglas@4cleanair.org; Roy Owens; Gary Rubenstein; frank.jarke@ps.ge.com; Cliff Glowacki; Michael.Klein@dep.state.nj.us; Segall.Robin@epamail.epa.gov; Bill Walker; Walt Smith; Leslie Ritts; Christopher Van Atten; Randy Bower; Michael Palazzolo; Jerry Fulmer; Jeffrey Lettrich; Patricia Strabbing; Mary Snow-Cooper; Kathleen Hennessey; Debby Rowe; WCGRAY@mactec.com; Marc Deslauriers; Shine.Brenda@epamail.epa.gov; Bruce Steiner; Steve McDaniel; Mark Lutrzkowski; Jeff Hege; linak.bill@epamail.epa.gov; Danny Greene; Joseph Martini; Jeffrey Rogers; Gary.Helm@Conectiv.com; JSchultz@steel.org; wreistad@tristategt.org; ValmontH@kochind.com; George.Marson@ec.gc.ca; Cory Wind; Art Werner; rshigehara@mindspring.com; Ralph Roberson; bobfinken@deltaaqs.com; Foley.Patrick@epamail.epa.gov; Krishna.Row@fhr.com; William Prokopy; Ray.Merrill@erg.com; BOConnor@paprican.ca; lfreeman@hunton.com; l_carlson@src-ncasi.org; Ashok Jain; drhoades@cleanair.com; jchaffee@bison-eng.com; Chad Whiteman; dfoerter@icac.com; Steve Eckard; Schell.Bob@epamail.epa.gov; Gary Fore; gary.napp@enviromet.net; BSANDSTR@indygov.org; Sue Anne Sheya; Mikel.Dennisk@epamail.epa.gov; Jim Serne; DCLINE@dem.state.in.us; David Leith; klimkowiczl@firstenergycorp.com; keredinger@babcock.com
Subject: Feb 9 meeting to discuss improved condensable PM test method

I look forward to our second meeting to discuss improvements in the condensable particulate matter testing methods. As the project progresses, I am getting more enthusiastic about the advantages of stakeholder interest and commitment to improve the test method and the

estimates of these emissions. As you can see from the draft meeting agenda, we have a full day planned.

The meeting will be in Room C114 at EPA's Research Triangle Park Campus. If you are flying in, you will want to arrive at Raleigh Durham International airport. The campus is less than 15 minutes from the airport even at rush hours. I have attached a file that provides directions to the campus and has two small maps. For those that cannot attend in person I have arranged a conference line so you can participate. The conference phone number is (919) 541-1590. If you have difficulties please call me (I will forward my phone to someone that can help you).

If you will be attending in person, please e-mail Ray Merrill and me so we can insure that EPA's security staff facilitate your access to the building. If you will have a laptop PC, you will need to fill out the attached form for the security staff. If you will participate through the conference line, please e-mail Ray Merrill and me so that I can insure that we have enough connections.

Here is the tentative agenda and schedule for the day.
(See attached file: 020907 meeting agenda rev 1-31-07.pdf)

You will notice that the meeting starts at 9:00 with presentations and is not over till 4:30. I know my earlier e-mail stated that I planed to start the meeting at 9:00 am with an unstructured mixer where coffee and breakfast snack will be provided. Also, I thought the meeting could end by 3:00. Unfortunately, we have a very full day and need to start the meeting earlier and continue a little later. I will still provide the coffee and breakfast snack but I hope you can forgo the mixer or get here a little earlier. For those wishing a more substantial fare, you can purchase an excellent breakfast at EPA's cafeteria which is adjacent to our meeting room. For those that have not made your travel arrangements I have attached links to the Raleigh Durham Airport and a listing of hotels near our office. If you need additional information to arrange your travel, please contact me and I will try to help you.

http://www.epa.gov/rtp/facilities/virtualtour/index.htm
http://www.rdu.com/
http://www.point-travel.com/durham/hotels-research-triangle-park-all.htm

(See attached file: EPA RTP campus directions.pdf)(See attached file: laptop pc checkin.pdf)

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Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards Sector Policy and Programs
Division Monitoring Policy Group, D243-05 RTP NC 27711 Tel. 919.541.5407
Fax 919.541.1039 E-mail myers.ron@epa.gov

**From:** "Roger Shigehara" <rshigehara@mindspring.com> ***Index 14***
**To:** <Myers.Ron@epamail.epa.gov>, <PMUELLER@epri.com>, <gaburn@mde.state.md.us>, <Huntley.Roy@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Parker.Barrett@epamail.epa.gov>, <Westlin.Peter@epamail.epa.gov>, <Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov>, <Oldham.Conniesue@epamail.epa.gov>, <marksh@kochind.com>, <Sorrell.Candace@epamail.epa.gov>, <ewstewart@mactec.com>, <glenn.england@ge.com>, "'Garry Brooks'" <garry.brooks@erg.com>, "'John Richards'" <john.richards@aircontroltechniques.com>, <mdmaret@mactec.com>, <shannon.vogel@ncmail.net>, <Driscoll.Tom@epamail.epa.gov>, <ngoodman@epri.com>, "'Dominic Cianciarelli'" <Dominic.Cianciarelli@ec.gc.ca>, <hschiff@trcsolutions.com>, "'Joe Fanjoy'" <joe.fanjoy@erg.com>, <Hardin.Erik@epamail.epa.gov>, <seebea@dnr.state.wi.us>, <mstewartdouglas@4cleanair.org>, "'Roy Owens'" <roy.owens@owenscorning.com>, "'Gary Rubenstein'" <grubenstein@sierraresearch.com>, <frank.jarke@ps.ge.com>, "'Cliff Glowacki'" <covenantassociates@columbus.rr.com>, <Michael.Klein@dep.state.nj.us>, <Segall.Robin@epamail.epa.gov>, "'Bill Walker'" <bwalker@cleanair.com>, "'Walt Smith'" <walt@waltersmith.com>, "'Leslie Ritts'" <lsritts@gmail.com>, "'Christopher Van Atten'" <vanatten@mjbradley.com>, "'Randy Bower'" <randy.bower@erg.com>, "'Michael Palazzolo'" <michael.palazzolo@alcoa.com>, "'Jerry Fulmer'" <jbfulmer@aol.com>, "'Jeffrey Lettrich'" <jeffrey.lettrich@alcoa.com>, "'Patricia Strabbing'" <pas2@daimlerchrysler.com>, "'Mary Snow-Cooper'" <ms14@daimlerchrysler.com>, "'Kathleen Hennessey'" <kmh17@daimlerchrysler.com>, "'Debby Rowe'" <das24@daimlerchrysler.com>, <WCGRAY@mactec.com>, "'Marc Deslauriers'" <Marc.Deslauriers@ec.gc.ca>, <Shine.Brenda@epamail.epa.gov>, "'Bruce Steiner'" <BruceS@steel.org>, "'Steve McDaniel'" <asmcdaniel@aqm.co.knox.tn.us>, "'Mark Lutrzkowski'" <Mark.Lutrzykowski@state.de.us>, "'Jeff Hege'" <jhege@indygov.org>, <linak.bill@epamail.epa.gov>, "'Danny Greene'" <Danny.Greene@erg.com>, "'Joseph Martini'" <joseph.martini@state.de.us>, "'Jeffrey Rogers'" <jeffrey.rogers@state.de.us>, <Gary.Helm@Conectiv.com>, <JSchultz@steel.org>, <wreistad@tristategt.org>, <ValmontH@kochind.com>, <George.Marson@ec.gc.ca>, "'Cory Wind'" <wind.cory@deq.state.or.us>, "'Art Werner'" <ASWerner@mactec.com>, "'Ralph Roberson'" <roberson@rmb-consulting.com>, <bobfinken@deltaaqs.com>, <Foley.Patrick@epamail.epa.gov>, <Krishna.Row@fhr.com>, "'William Prokopy'" <wrp6@daimlerchrysler.com>, <Ray.Merrill@erg.com>, <BOConnor@paprican.ca>, <lfreeman@hunton.com>, <l_carlson@src-ncasi.org>, "'Ashok Jain'" <AJain@src-ncasi.org>, <drhoades@cleanair.com>, <jchaffee@bison-eng.com>, "'Chad Whiteman'" <cwhiteman@icac.com>, <dfoerter@icac.com>, <steve.eckard@enthalpy.com>, <Schell.Bob@epamail.epa.gov>, "'Gary Fore'" <gfore@hotmix.org>, <gary.napp@enviromet.net>, <BSANDSTR@indygov.org>, "'Sue Anne Sheya'" <ssheya@technikonllc.com>, <Mikel.Dennisk@epamail.epa.gov>, "'Jim Serne'" <jserne@trcsolutions.com>, <DCLINE@dem.state.in.us>, "'David Leith'" <"david_leith%unc,edu"@epamail.epa.gov>, <klimkowiczl@firstenergycorp.com>, <keredinger@babcock.com>
**Date:** Wed, Feb 7, 2007 1:34 AM
**Subject:** RE: Feb 9 meeting to discuss improved condensable PM test method

Ron,
Thanks for the agenda for the 2/9/2007 meeting. From the agenda, it appears to me that EPA is forging ahead with the dry impinger train and has dropped any considerations to other alternatives. To date, the preliminary experiments have shown that the dry train gives less than 1 mg artifact and the wet train about 10 mg. The results are for 150 ppm SO2 concentrations and 10% moisture. This is encouraging, but the effect of ammonia and on the organic fraction is still unknown.

The analysis of pre-dry sulfates indicates that there might be a problem. Either the analytical method is inaccurate or sulfates are being lost (at low levels) and gained (at high levels) in the drying process.

No experiments have been done with ammonia and its effect on artifacts. Some studies have proceeded at maintaining a higher coil temperature not considering the impact it might have on organics. My understanding is that

the preliminary results indicate higher moisture content in the silica gel (30-40% rather than 4% when the ice bath is used).

EPA apparently is not considering the following in its future experiments or approach:

Use of a separate method for SO3, using the controlled condensation method or modified Method 8 (method with a prefilter for PM solids) or analyzing for sulfates (assuming that SO3 is the only significant inorganic condensable). The latter would meet the goal of using one sampling train for both organics and inorganics.

Use of HCl with reduced reagent volume in impingers.

There are several stakeholder presentations. It would be great if we could get a brief summary and data for the presentations. My understanding is the Jorge Marson of Environment Canada has been doing substantial investigations, including the use of HCl. It would be great if we had a summary of the data before the meeting.

EPA's goal to have one method with few options and obtaining both organic and inorganic fractions in one train is noble, but it is best not to place road blocks when simpler solutions might be available.

Looking forward to the meeting.

Roger S.

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Wednesday, January 31, 2007 6:48 PM
To: PMUELLER@epri.com; gaburn@mde.state.md.us; Huntley.Roy@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Parker.Barrett@epamail.epa.gov; Westlin.Peter@epamail.epa.gov; Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov; Oldham.Conniesue@epamail.epa.gov; marksh@kochind.com; Sorrell.Candace@epamail.epa.gov; ewstewart@mactec.com; glenn.england@ge.com; Garry Brooks; John Richards; mdmaret@mactec.com; shannon.vogel@ncmail.net; Driscoll.Tom@epamail.epa.gov; ngoodman@epri.com; Dominic Cianciarelli; hschiff@trcsolutions.com; Joe Fanjoy; Hardin.Erik@epamail.epa.gov; seebea@dnr.state.wi.us; mstewartdouglas@4cleanair.org; Roy Owens; Gary Rubenstein; frank.jarke@ps.ge.com; Cliff Glowacki; Michael.Klein@dep.state.nj.us; Segall.Robin@epamail.epa.gov; Bill Walker; Walt Smith; Leslie Ritts; Christopher Van Atten; Randy Bower; Michael Palazzolo; Jerry Fulmer; Jeffrey Lettrich; Patricia Strabbing; Mary Snow-Cooper; Kathleen Hennessey; Debby Rowe; WCGRAY@mactec.com; Marc Deslauriers; Shine.Brenda@epamail.epa.gov; Bruce Steiner; Steve McDaniel; Mark Lutrzkowski; Jeff Hege; linak.bill@epamail.epa.gov; Danny Greene; Joseph Martini; Jeffrey Rogers; Gary.Helm@Conectiv.com; JSchultz@steel.org; wreistad@tristategt.org; ValmontH@kochind.com; George.Marson@ec.gc.ca; Cory Wind; Art Werner; rshigehara@mindspring.com; Ralph Roberson; bobfinken@deltaaqs.com; Foley.Patrick@epamail.epa.gov; Krishna.Row@fhr.com; William Prokopy; Ray.Merrill@erg.com; BOConnor@papricanca; lfreeman@hunton.com; l_carlson@src-ncasi.org; Ashok Jain; drhoades@cleanair.com; jchaffee@bison-eng.com; Chad Whiteman; dfoerter@icac.com; steve.eckard@enthalpy.com; Schell.Bob@epamail.epa.gov; Gary Fore; gary.napp@enviromet.net; BSANDSTR@indygov.org; Sue Anne Sheya; Mikel.Dennisk@epamail.epa.gov; Jim Serne; DCLINE@dem.state.in.us; David

Leith; klimkowiczl@firstenergycorp.com; keredinger@babcock.com
Subject: Feb 9 meeting to discuss improved condensable PM test method

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http://www.epa.gov/rtp/facilities/virtualtour/index.htm
http://www.rdu.com/
http://www.point-travel.com/durham/hotels-research-triangle-park-all.htm

(See attached file: EPA RTP campus directions.pdf)(See attached file: laptop pc checkin.pdf)

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Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05

RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

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***Index 15***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Fri, Feb 16, 2007 4:19 PM
**Subject:** Drying aqueous solutions by evaporation

Hi Ray,

Some thoughts on M 202 condensate drying. I will try your drying agent suggestions, and will keep you posted on the "test the driers" tests.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

**EVAPORATION DRYING OF SULPHURIC ACID SOLUTIONS**

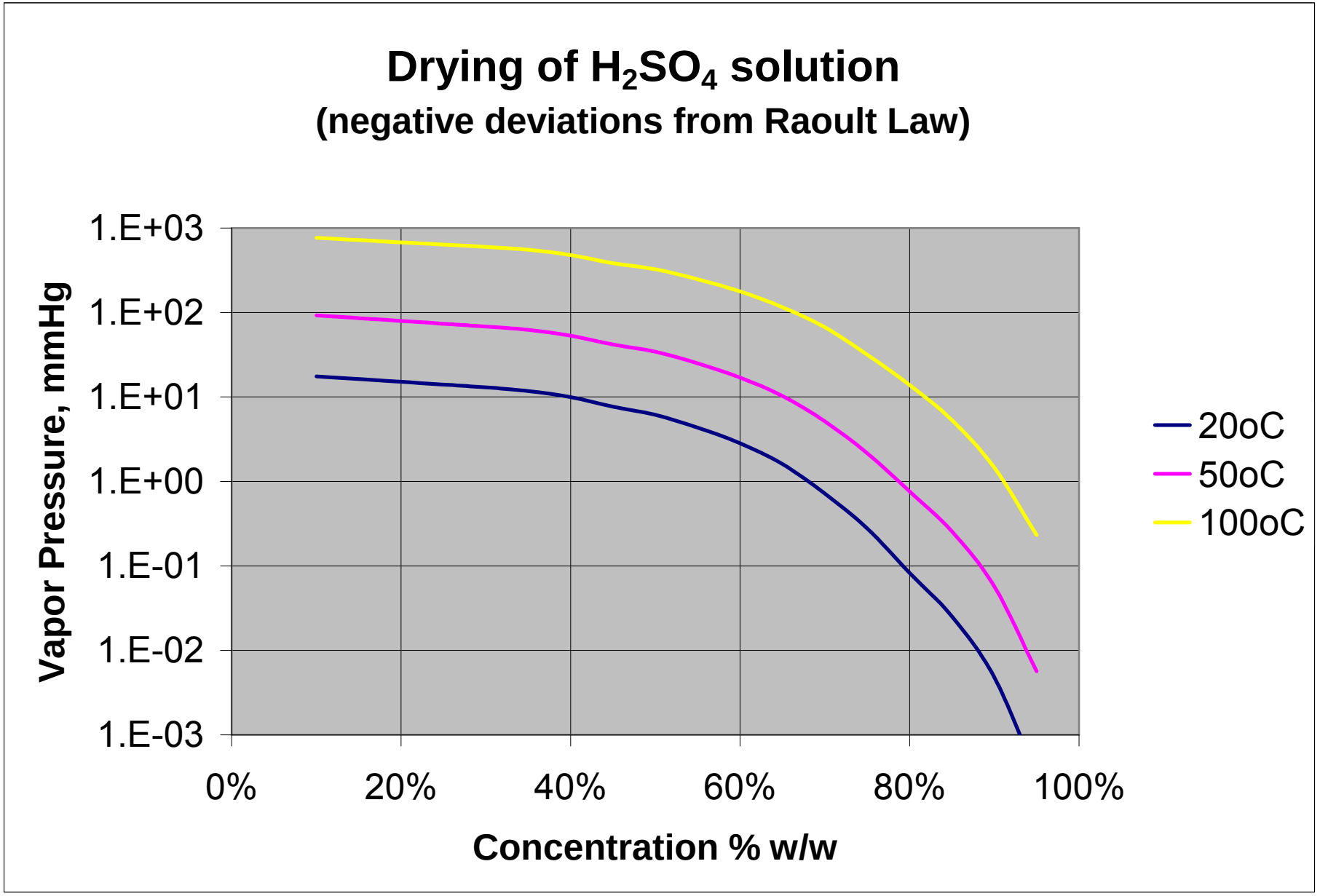
| **Source Conditions** | Stage 1 | Stage 2 | | | | data entry |
|---|---|---|---|---|---|---|
| Drying temperature, oC | **50** | **30** | | | | |
| Sample volume, ml | **20** | | | | | |
| Acid weight, mg | **20** | | | | | |
| Sample weight at end of stage 1, mg | **200** | | | | | |
| Acid concentration, % w/w | 10% | 30% | 35% | 40% | 45% | 50% |
| A * | 8.1393986 | 8.864 | 8.873 | 8.844 | 8.809 | 8.832 |
| B * | 1767.262 | 2271 | 2286 | 2299 | 2322 | 2357 |
| C** | 236.29 | | | | | |
| Vapour pressure, mmHg | 93 | 23 | 21 | 18 | 14 | 11 |
| Initial weight, mg | 20,000 | 200 | 57 | 50 | 44 | 40 |
| Residue weight, mg | 200 | 57 | 50 | 44 | 40 | 36 |
| Drying rate, mg/min *** | 27.0 | 6.8 | 6.2 | 5.3 | 4.1 | 3.3 |
| Drying time per stage, minutes | 733.8 | 2.1E+01 | 1.2E+00 | 1.1E+00 | 1.1E+00 | 1.1E+00 |
| Sample residue bias, % | | | | | | |
| Cumulative drying time, hours | 12.2 | 12.6 | 12.6 | 12.6 | 12.6 | 12.7 |

** A and B parameters from Perry's 4th. Ed., Table 3-13*

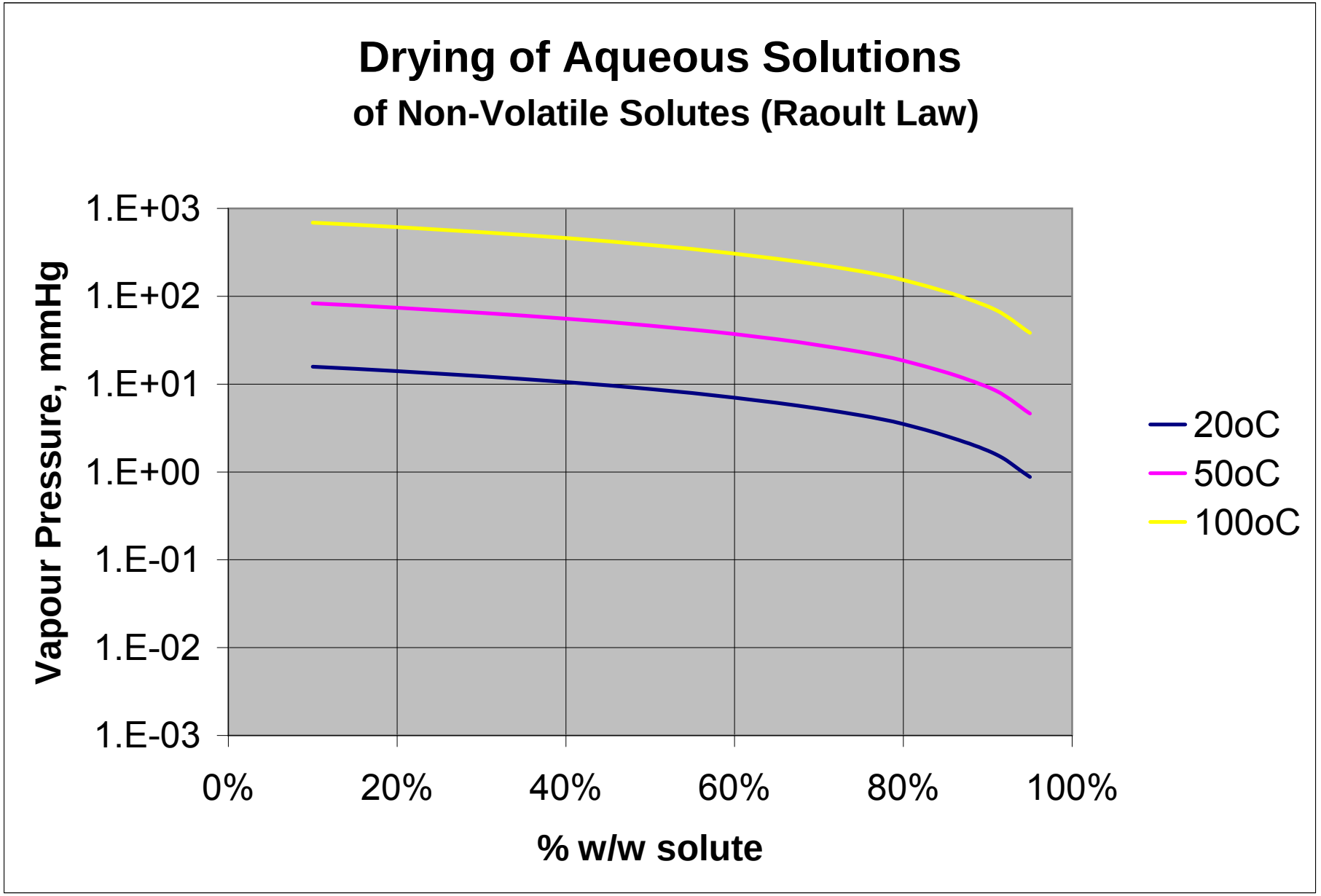
*** A,B,C parameters for water (30-50 $^{o}$ C range) from API Research project 44, Oct 1962,*

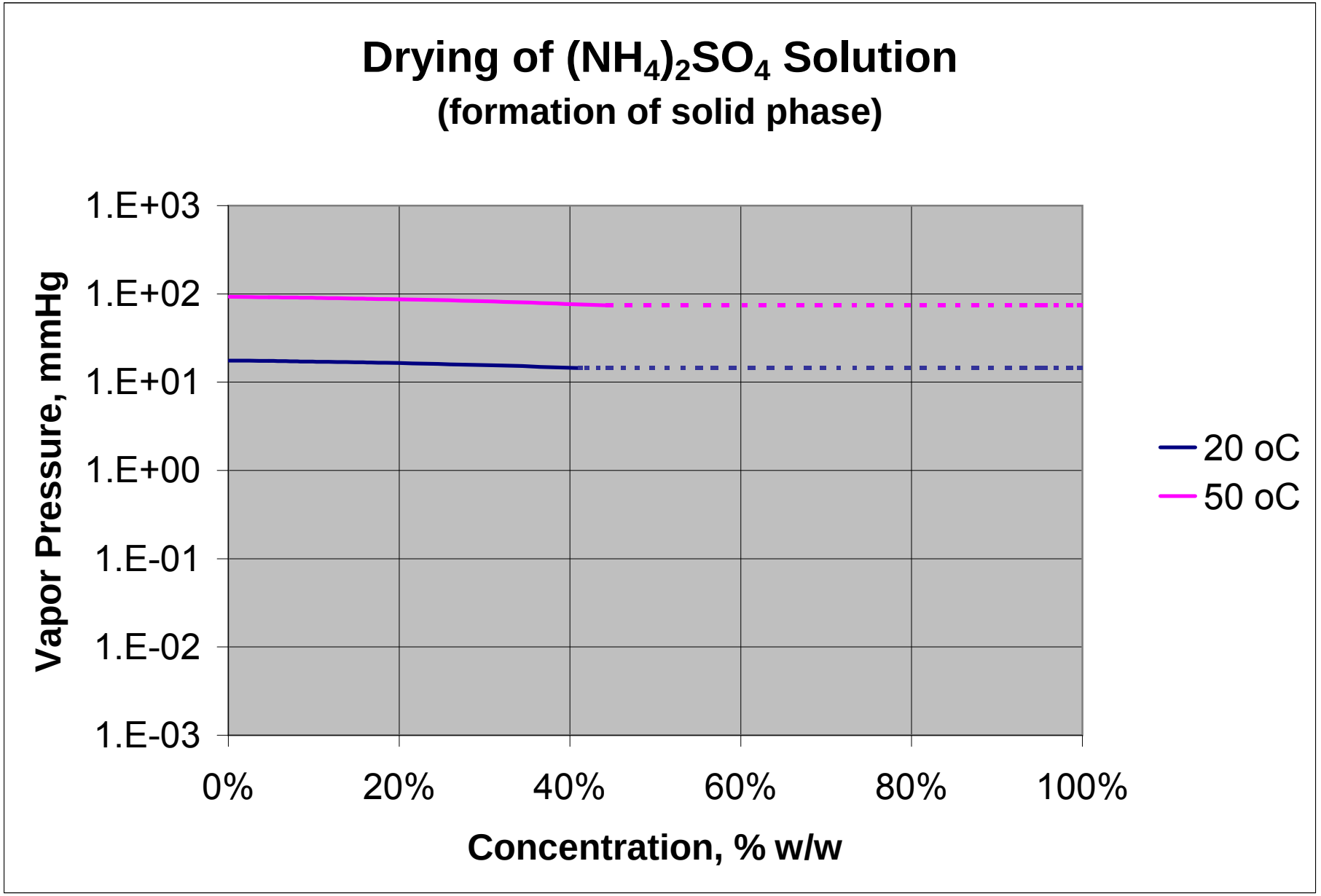
**** extrapolated from 5.6 cm diameter water drying pan experiments at 22 $^{o}$ C*

| 55% | 60% | 65% | 70% | 75% | 80% | 85% | 90% | 95% |
|---|---|---|---|---|---|---|---|---|
| 8.827 | 8.841 | 8.853 | 9.032 | 9.034 | 9.293 | 9.239 | 9.255 | 9.79 |
| 2400 | 2458 | 2533 | 2688 | 2810 | 3040 | 3175 | 3390 | 3888 |
| | | | | | | | | |
| 8 | 5 | 3 | 1 | 0.5755 | 0.1820 | 0.0576 | 0.0117 | 0.0009 |
| 36 | 33 | 31 | 29 | 27 | 25 | 24 | 22 | 21 |
| 33 | 31 | 29 | 27 | 25 | 24 | 22 | 21 | |
| 2.3 | 1.6 | 0.9 | 0.4 | 1.7E-01 | 5.3E-02 | 1.7E-02 | 3.4E-03 | 2.6E-04 |
| 1.3E+00 | 1.6E+00 | 2.4E+00 | 4.5E+00 | 9.9E+00 | 2.8E+01 | 7.8E+01 | 3.4E+02 | |
| | | | | **25%** | **18%** | **11%** | **5%** | |
| 12.7 | 12.7 | 12.7 | 12.8 | 13.0 | 13.4 | 14.7 | **20.5** | |


Drying of $H_2SO_4$ solution
(negative deviations from Raoult Law)
Vapor Pressure, mmHg
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
0%
20%
40%
60%
80%
100%
Concentration % w/w
20oC
50oC
100oC

Sulphuric acid **does not form a separate phase** as water is lost.
The vapour pressure of the solution drops substantially when the concentratior raises above 50%. Extremely dry air is necessary to concentrate the acid to > 90% level (< 0.01 mmHg water VP at 20$^{o}$C) and a bias remains unless the air is absolutely dry.
Similar considerations apply to any other pair of liquids that are fully miscible.


Drying of Aqueous Solutions
of Non-Volatile Solutes (Raoult Law)
Vapour Pressure, mmHg
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
0%
20%
40%
60%
80%
100%
% w/w solute
20oC
50oC
100oC


Drying of (NH4)2SO4 Solution
(formation of solid phase)
Vapor Pressure, mmHg
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
0%
20%
40%
60%
80%
100%
Concentration, % w/w
20 oC
50 oC

Weighing of ammonia sulphate is preferrable to that of sulphuric acid because:
1) a solid phase is formed when solution concentration gets higher than 40%
2) this allow the loss of water without further concentration of the solution
3) the vapour pressure of the solution remains >10 mmHg until the end
4) the positibe weight bias can be avoided.

**EVAPORATION DRYING OF AMMONIA SULPHATE SOLUTIONS**

| **Source Conditions** | Stage 1 | Stage 2 | | | | data entry |
|---|---|---|---|---|---|---|
| Drying temperature, oC | **50** | **30** | | | | |
| Sample volume, ml | **20** | | | | | |
| Salt weight, mg | **20** | | | | | |
| Sample weight at end of stage 1, mg | **200** | | | | | |
| Water vapour pressure Antoine parameters | | | | | | |
| A ** | 8.1393986 | | | | | |
| B ** | 1767.262 | | | | | |
| C** | 236.29 | | | | | |
| Vapour pressure (VP) of water, mmHg | 93 | | | | | |
| Solution concentration, % w/w | 10% | | | | | |
| Solution concentration, g/100g $H_2O$* | | 5 | 10 | 20 | 30 | 40 |
| Solution concentration, % w/w | 10.0% | 4.8% | 9.1% | 16.7% | 23.1% | 28.6% |
| Solution VP @ 10 $^oC$, mmHg * | | 9.1 | 9.0 | 8.7 | 8.5 | 8.3 |
| Solution VP @ 20 $^oC$, mmHg * | | 17.4 | 17.1 | 16.7 | 16.2 | 15.7 |
| Solution VP @ 30 $^oC$, mmHg * | | 31.5 | 31.1 | 30.3 | 29.4 | 28.6 |
| Solution VP @ 40 $^oC$, mmHg * | | 54.7 | 54.1 | 52.6 | 51.1 | 49.6 |
| Solution VP @ 50 $^oC$, mmHg * | | 91.5 | 90.4 | 87.9 | 85.5 | 83.0 |
| VP at selected temp., mmHg | 93 | 31.5 | 31.1 | 30.3 | 29.4 | 28.6 |
| Initial weight, mg | 20,000 | 200 | 105 | 57 | 41 | 33 |
| Residue weight, mg | 200 | 105 | 57 | 41 | 33 | 29 |
| Drying rate, mg/min *** | 27.0 | 9.2 | 9.1 | 8.8 | 8.6 | 8.3 |
| Drying time per stage, minutes | 734 | 10.4 | 5.3 | 1.8 | 0.9 | 0.6 |
| Sample residue bias, % | | | | | | 43% |
| Cumulative drying time, hours | 12.2 | 12.4 | 12.5 | 12.5 | 12.5 | 12.5 |

** Vapour pressure data from US NRC, "International Critical Tables", Vol III, 1st. Edition, 1923*

*** A,B,C parameters for water (30-50 $^oC$ range) from API Research project 44, Oct 1962,*

**** extrapolated from 5.6 cm diameter water drying pan experiments at 22 $^oC$*

| 50 | 60 | 70 | 80 | 300 | 2000 | 3000 |
|---|---|---|---|---|---|---|
| 33.3% | 37.5% | 41.2% | 44.4% | 75.0% | 95.2% | 96.8% |
| 8.0 | 7.8 | 7.6 | | | | |
| 15.3 | 14.8 | 14.4 | | | | |
| 27.7 | 26.9 | 26.2 | | | | |
| 48.2 | 46.8 | 45.5 | 44.2 | | | |
| 80.6 | 78.3 | 76.1 | 73.9 | | | |
| 27.7 | 26.9 | 26.2 | 0.0 | 0.0 | 0.0 | |
| 29 | 25 | 23 | 21 | 20 | 20 | |
| 25 | 23 | 21 | 20 | 20 | 20 | |
| 8.1 | 7.8 | 7.6 | 7.6 | 7.6 | 7.6 | |
| 0.4 | 0.3 | 0.2 | 0.2 | 0.0 | 0.0 | |
| 27% | 16% | 7% | **0%** | | | |
| 12.6 | 12.6 | 12.6 | **12.6** | | | |

***Index 16***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Tue, Feb 20, 2007 10:44 AM
**Subject:** RE: Drying aqueous solutions by evaporation

Hi Ray;

Neither silicagel desiccators nor dryerite desiccators can concentrate sulphuric acid solutions to higher than 70% w/w level, which corresponds to 1 mmHg water vapor pressure, approximately. Therefore the ammonia neutralization step should be a mandatory step in Method 202.

I will continue experimenting with drying aqueous solutions of target compounds (glycerol, benzoic acid, adipic acid, etc.)

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

-----Original Message-----
From: Ray Merrill [mailto:Ray.Merrill@erg.com]
Sent: Friday, February 16, 2007 4:25 PM
To: Marson, George (Jorge) [ETC]
Subject: Re: Drying aqueous solutions by evaporation

I've put our OMEGA RH probe in an unused desiccator, I'll let you know what it reads after equilibration. I'll be it's no better than 15% RH
Ray

>>> "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca> 2/16/2007 4:13:22 PM >>>
Hi Ray,

Some thoughts on M 202 condensate drying. I will try your drying agent suggestions, and will keep you posted on the "test the driers" tests.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

***Index 17***

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Wed, Feb 21, 2007 2:28 PM
**Subject:** RE: Desiccator effectiveness.

Thank you, Ray

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

-----Original Message-----
From: Ray Merrill [mailto:Ray.Merrill@erg.com]
Sent: Wednesday, February 21, 2007 1:40 PM
To: Marson, George (Jorge) [ETC]
Cc: myers.ron@epa.gov
Subject: RE: Desiccator effectiveness.

Jorge

Here's the rest of the desiccator story.
I wrote earlier that the active indicator silica desiccant dropped the relative humidity to about 28% in our desiccators. Indicating calcium sulfate desiccant dropped the relative humidity to 13%.
EPA's method 202 specifies calcium sulfate and now we may know the reason.

Ray

>>> "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca> 2/20/2007 10:35 AM >>>
Hi Ray;

Neither silicagel desiccators nor dryerite desiccators can concentrate sulphuric acid solutions to higher than 70% w/w level, which corresponds to 1 mmHg water vapor pressure, approximately. Therefore the ammonia neutralization step should be a mandatory step in Method 202.

I will continue experimenting with drying aqueous solutions of target compounds (glycerol, benzoic acid, adipic acid, etc.)

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To: Marson, George (Jorge) [ETC]
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Hi Ray,

Some thoughts on M 202 condensate drying. I will try your drying agent suggestions, and will keep you posted on the "test the driers" tests.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

**Ray Merrill - Desiccator results**

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca> ***Index 18***
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** 2/27/2007 9:54 AM
**Subject:** Desiccator results

Ray,

Sharing the latest desiccator ("Dryerite") results.

Each determination was done in triplicate pairs (3 "pure CPM" pans, 3 "diluted CPM" pans). I'am awaiting arrival of a bunch of a few other CPM chemicals to test.

**Summary Desiccator Drying Experiments, Feb. 07**

| CPM | | Solvent | Combined losses * | | CPM losses ** | | CPM conc. |
|---|---|---|---|---|---|---|---|
| name | mg. Avg. | name | mg/hr | %/hr | mg/hr | %/hr | after 24 hrs |
| n-pentadecane | 79 | $MeCl_2$ | -500 *** | - | -0.05 | -0.07% | 100% |
| n-hexadecane | 24 | $MeCl_2$ | -500 *** | - | -0.07 | -0.28% | 100% |
| phenanthrene | 17 | $MeCl_2$ | -500 *** | - | -0.04 | -0.25% | 100% |
| $CH_3COOH$ | 88 | water | -24.1 | -6.8% | -5.97 | -6.39% | full loss |
| HCL | 59 | water | -25.8 | -6.2% | -10.99 | -6.62% | full loss |
| $HNO_3$ | 99 | water | -19.5 | -5.1% | -8.91 | -6.43% | full loss |
| Glycerol | 75 | water | -31.7 | -12.6% | -0.03 | -0.05% | 100% |
| $NH_4Cl$ | 22 | water | -29.6 | -10.2% | -0.05 | -0.24% | 100% |
| $(NH_4)_2SO_4$ | 210 | water | -35.8 | -4.6% | 0.02 | 0.01% | 100% |
| $H_2SO_4$ | 148 | water | -17.6 | -3.0% | -0.62 | -0.40% | ~73% |

* from 10-50% CPM pans **from 100% CPM pans *** estimated value

The H2SO4 end point is shaky (-0.40 %/hr loss) but after 24 hr there is convergence between "pure CPM" pans and the "diluted CPM" pans at approx. 73% w/w H2SO4 calculated concentration.

Ammonia neutralization would "fix" acids (HCl, NO3, CH3COOH) that are otherwise volatile.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032

**Index 19**

**From:** "Marson, George (Jorge) [ETC]" <George.Marson@ec.gc.ca>
**To:** "Ray Merrill" <Ray.Merrill@erg.com>, <Myers.Ron@epamail.epa.gov>
**Date:** Wed, Feb 28, 2007 3:14 PM
**Subject:** Drying aqueous solutions by evaporation

Hi Ray,

I repeated and extended some CPM drying runs, and here it is a summary of the results.

CPM

Solvent

Interval

CPM losses

Final

name

mg

name

hours

%/hr

CPM

Phenanthrene

18

MeCl2

16 to 24

-1.11%

100%

n-tetradecane

210

MeCl2

23 to 41

-0.60%

100%

n-pentadecane

78

MeCl2

24 to 46

-0.15%

100%

n-hexadecane

191

MeCl2

18 to 24

-0.11%

100%

Glycerol

76

water

16 to 24

-0.65%

100%

HNO3

147

water

15 to 24

full loss

-

CH3COOH

83

water

15 to 24

full loss

-

HCl

149

water

15 to 24

full loss

-

H3PO4

181

water

23 to 41

0.03%

~88%

H2SO4

136

water

23 to 41

-0.30%

~71%

NH4Cl

21

water

16 to 24

-0.83%

100%

(NH4)2SO4

208

water

24 to 46

-0.05%

100%

Regards

George Marson, P.Eng.

QA & EMS Supervisor

phone (613) 991-9458

fax (613) 998-4032

-----Original Message-----
From: Ray Merrill [mailto:Ray.Merrill@erg.com]
Sent: Friday, February 16, 2007 4:25 PM
To: Marson, George (Jorge) [ETC]
Subject: Re: Drying aqueous solutions by evaporation

I've put our OMEGA RH probe in an unused desiccator, I'll let you know

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Hi Ray,

Some thoughts on M 202 condensate drying. I will try your drying agent

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Regards

George Marson, P.Eng.

QA & EMS Supervisor

phone (613) 991-9458

fax (613) 998-4032

**CC:** "Cianciarelli,Dominic [ETC]" <Dominic.Cianciarelli@ec.gc.ca>

***Index 20***

**From:** <Myers.Ron@epamail.epa.gov>
**To:** Michael Klein <Michael.Klein@dep.state.nj.us>
**Date:** Wed, Mar 14, 2007 2:30 PM
**Subject:** Re: M202 blanks

Mike:
I don't remember talking about volume correcting blanks. For Gary, Ray and my education, what specifically do you mean by volume correcting. Would I be correct in assuming that it is determining the volumes of MeCl and acetone used to determine the mass for blanks and the volumes of MeCl and acetone used to recover the sample in the field and to extract the organic condensable PM and using the relative volumes to subtract the mass of material in the solvents used for sample recovery and extraction?

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

Michael Klein
<Michael.Klein@dep.state.nj.us>
03/14/2007 10:40 AM

To: Ron Myers/RTP/USEPA/US@EPA
cc:
Subject: M202 blanks

Ron - I'm pretty sure I talked to you about this a long time ago, but the current method implies, but does not explicitly detail procedures for volume correcting the blanks. I have a lab trying to argue with me that they don't need to do it, even though it is common sense. Just wanted to mention it again for when you're doing the revised RM202 so this gets updated as well. Thanks.

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

**CC:** <Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov>, <Ray.Merrill@erg.com>

**From:** "Michael Klein" <Michael.Klein@dep.state.nj.us> ***Index 21***
**To:** <Myers.Ron@epamail.epa.gov>
**Date:** Wed, Mar 14, 2007 2:47 PM
**Subject:** Re: M202 blanks

Yes, analogous to EPA5, Eqn. 5-4 & 5-5 (though we don't bother with the density since it cancels out).

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

>>> <Myers.Ron@epamail.epa.gov> 3/14/2007 2:26 PM >>>
Mike:
I don't remember talking about volume correcting blanks. For Gary, Ray and my education, what specifically do you mean by volume correcting. Would I be correct in assuming that it is determining the volumes of MeCl and acetone used to determine the mass for blanks and the volumes of MeCl and acetone used to recover the sample in the field and to extract the organic condensable PM and using the relative volumes to subtract the mass of material in the solvents used for sample recovery and extraction?

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RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

Michael Klein
<Michael.Klein@dep.state.nj.us>
03/14/2007 10:40 AM

To
Ron Myers/RTP/USEPA/US@EPA
cc
Subject
M202 blanks

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Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

**CC:** <Ray.Merrill@erg.com>, <Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov>

**From:** "Michael Klein" <Michael.Klein@dep.state.nj.us> ***Index 22***
**To:** <myers.ron@epa.gov>
**Date:** Wed, Mar 14, 2007 3:08 PM
**Subject:** Fwd: Re: M202 blanks

Sending this again because Gary's e-mail address was rejected. Sending to all just in case.

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

>>> Michael Klein 3/14/2007 2:41 PM >>>
Yes, analogous to EPA5, Eqn. 5-4 & 5-5 (though we don't bother with the density since it cancels out).

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

>>> <Myers.Ron@epamail.epa.gov> 3/14/2007 2:26 PM >>>
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Fax 919.541.1039
E-mail myers.ron@epa.gov

Michael Klein
<Michael.Klein@d
ep.state.nj.us> To
Ron Myers/RTP/USEPA/US@EPA
03/14/2007 10:40 cc
AM
Subject
M202 blanks

Ron - I'm pretty sure I talked to you about this a long time ago, but the current method implies, but does not explicitly detail procedures for volume correcting the blanks. I have a lab trying to argue with me that they don't need to do it, even though it is common sense. Just wanted to mention it again for when you're doing the revised RM202 so this gets updated as well. Thanks.

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

**CC:** <mcalister.gary@epa.gov>, <Ray.Merrill@erg.com>

**From:** Ray Merrill ***Index 23***
**To:** Klein, Michael; myers.ron@epa.gov
**Date:** Wed, Mar 14, 2007 3:55 PM
**Subject:** Fwd: Re: M202 blanks

Michael and Ron

Thanks for including me in the cc list on this email. Ron and I are working on the revision to the condensable particulate method.

Here's my thoughts for you to consider. The volume specified for the reagent blanks is nominally the same as we expect sampling firms to use in the field. As written M-202 specifies the amount of water to be added into the cold impingers and the blank results should be corrected for the actual volume used.

If the blank values are low, which they should be if the sampling firm used quality reagents and didn't contaminate them in the field, then the impact of not correcting for the volume used small. If the blank in 100 mL is large and the sampling firm used 300 mL or more then the correction could be off by a factor of 3. However, not correcting for the additional blank solvent volume could bias the results high and penalize the regulated source.

Alternatively, if the organic blank is high and the volume used for the organic rinse is small, then the volume correction could reduce the blank contribution. Not correcting the train results for smaller volume of organic reagent (smaller than used to determine the blank) could bias the results low and reward the regulated source.

Ron and Gary should comment on the policy aspects of this issue.

We have seen significant blank issues from stakeholders for both water and organic solvents. You probably know that our recent work for Ron and EPA, the organic reagent blank is ~ zero, and the water blank is ~0.2 milligram in 100 mL.

Hope this helps

Ray Merrill
Eastern Research Group
919 468-7887

>>> "Michael Klein" <Michael.Klein@dep.state.nj.us> 3/14/2007 2:46 PM >>>
Sending this again because Gary's e-mail address was rejected. Sending to all just in case.

Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

>>> Michael Klein 3/14/2007 2:41 PM >>>
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michael.klein@dep.state.nj.us

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Monitoring Policy Group, D243-05
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Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

Michael Klein
<Michael.Klein@dep.state.nj.us>
03/14/2007 10:40 AM

To: Ron Myers/RTP/USEPA/US@EPA
cc:
Subject: M202 blanks

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Michael A. Klein
NJDEP - BTS
michael.klein@dep.state.nj.us

**CC:** mcalister.gary@epa.gov; Merrill, Ray

**From:** <Myers.Ron@epamail.epa.gov> ***Index 24***
**To:** <Ray.Merrill@erg.com>
**Date:** Mon, Apr 2, 2007 10:08 AM
**Subject:** Fw: FHR would like to proceed with modified M202 engineering analysis

Ray:
My mind must be going as I was sure that I had you on the CC list.

ALSO, I saw that the work assignment change got signed on Friday. See below:
(See attached file: signed 68D02079 WA 5-03-2.pdf)

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

----- Forwarded by Ron Myers/RTP/USEPA/US on 04/02/2007 09:57 AM -----

| | | |
|---|---|---|
| Ron Myers/RTP/USEPA/US<br>03/30/2007 04:40 PM | To | "Row, Krishna" <Krishna.Row@fhr.com> |
| | cc | curtis.stock@pca.state.mn.us, "Krautkremer, Michael" <Michael.Krautkremer@fhr.com> |
| | Subject | Re: FHR would like to proceed with modified M202 engineering analysis(Document link: Ron Myers) |

Krishna:
As we discussed in our phone conversation, I just received the draft test method from my contractor for my review. It is attached below. I have not yet completely reviewed the attached in detail. I have performed a cursory evaluation and it appears consistent with what we think will work. This is the procedure that we used in our laboratory study. I have shared this with another test contractor that is working for a stakeholder and performed a test this last week (I hope). You will notice that the vast majority of pages in the method are devoted to

the in stack particle sizing for PM10 and PM2.5. Since you are testing a gas fired source, it is reasonable to conclude that all of the particulate is sub-micrometer in size and you would not need to use the cyclones in your testing. I would hope that you could perform the tests that you plan using paired sampling trains (nozzles within 1" to 2" ). This would provide information on the precision of the method under the gas matrices generated by your process heater. As part of your participation in this stakeholder process, you should probably review our Quality Assurance Project Plan for the laboratory study ( http://www.epa.gov/ttn/emc/methods/m202doc6.pdf ), have your test contractor read the QAPP, complete an addendum to this plan (using the template at the end of the QAPP and follow those parts of our QAPP that would be appropriate for your field testing and those parts you provide in your addendum.

As another suggestion, we have developed an electronic source test planning and reporting tool that is available for beta testing. You and the State may want to use this tool to simplify and expedite the handling of the test information. The Electronic Reporting Tool (ERT) is available at http://www.epa.gov/ttn/chief/ert/ert_tool.html . The tool at the top of this web page is a version that has been available for over a year and was our first attempt. The tool at the bottom of the page is a beta version 3 which includes many other pollutants and includes an export function. I understand that you are already doing a lot of new procedures in this effort, but I don't think this will increase your contractors effort (and may decrease it for future tests), reduce your effort if you QA work by your contractors and will definitely decrease the work by the State agency if they recalculate one or more of the runs.

I have copied this to Ray Merrill {(919) 468-7887}, who is my contractor for the Method 202 improvement work and if you have questions (or comments) on the method and can't reach me can help you with the method and the QA component.

(See attached file: DRAFT Method 20X 3-19-07.pdf)

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

"Row, Krishna" <Krishna.Row@fhr.com> 03/29/2007 04:20 PM

To Ron Myers/RTP/USEPA/US@EPA

cc "Krautkremer, Michael" <Michael.Krautkremer@fhr.com>,

curtis.stock@pca.state.mn.us

Subject
FHR would like to proceed with modified M202 engineering analysis

Ron,
Mike Krautkremer met with Curt Stock of MPCA earlier this week to discuss the possibility of conducting the modified Method 202 engineering analysis at the next available opportunity on a process heater. Mr. Stock is receptive to the idea of conducting an engineering analysis using the "draft" version of this test. Please share a copy of the proposed test method with us, if possible. We appreciate your help.

Thank you,
Krishna Row
Senior Technical Advisor - Environmental
Pine Bend Refinery Flint Hills Resources
Phone: 651-437-0590
Fax : 651-437-0581

TN

| WORK ASSIGNMENT<br>ENVIRONMENTAL PROTECTION AGENCY<br>RESEARCH TRIANGLE PARK, NC 27711 | CONTRACT NO: 68-D-02-079<br>CONTRACTOR: ERG<br>ASSIGNMENT NO: 5-03<br>ASSIGNMENT CHANGE NO: 2 |
|---|---|
| **TITLE:** Method 202 Assessment & Evaluation for Bias and Other Uses | **DATE:** 3/31/07 |

**DESCRIPTION:**
See attached background and revised statement of work.

In addition, we are extending the duration of the work by an additional three months to perform the additional tasks identified in this work assignment change.

Also, to the best of our knowledge, this work does not duplicate any previous or current work being done by this office.

| ESTIMATE OF: | GOVERNMENT ESTIMATE: | | |
|---|---|---|---|
| LABOR HOURS | Change from 654 hours to 900 hours | CHANGE | |
| DURATION OF WORK | Change from 9 Months to 12 Months | CHANGE | |
| COMPLETION DATE | Change from 6/29/2007 to 9/28/2007 | CHANGE | |
| WORK ASSIGNMENT MANAGER:<br>Ron Myers Ronald L Myers | ORG CODE:<br>OAQPS/SPPD/MPG | TELEPHONE:<br>(919)541-0516 | DATE:<br>3/6/2007 |

| APPROVALS: | | DATE: |
|---|---|---|
| GROUP LEADER | Robert Schell R. Schell | 3/8/07 |
| PROJECT OFFICER | Valerie Graves Valerie Graves | 3/8/07 |
| CONTRACTING OFFICER | Otelia Newsome Otelia Newsome | 3/31/07 |

| CONTRACTOR'S REPRESENTATIVE ACKNOWLEDGMENT | | |
|---|---|---|
| SIGNATURE: | TITLE: | DATE: |

EPA (RTP) 395, REV 5/95

TN

**Method 202 Assessment & Evaluation for Bias and Other Uses**

Background

Emissions Inventories for the National Emissions Inventory (NEI), State Implementation Plans (SIPs) and the Consolidated Emissions Reporting Rule (CERR) require the reporting of primary particulate matter emissions including both the filterable and condensable components. The basis of emissions inventories is a combination of emissions factors and, when available, site-specific test results. Site-specific test results provide a direct measurement of emissions, emissions factors are estimates of emissions representing averages of several site-specific test results. Although emissions factors development and emissions inventory reporting depend of site-specific tests, the usual purpose for conducting the emissions test is to demonstrate compliance with an existing emissions limitation. The effective management of the ambient air quality requires that the NEI, the SIP emissions inventories, the periodic emissions inventories required under the CERR measurements and the results of compliance test reports be unbiased and with known uncertainty.

The test method most frequently used to quantify condensable particulate matter emissions is EPA Method 202 as published in Appendix M of 40CFR51. EPA Method 202, as promulgated in 1991, specifies collection of a representative sample in an arrangement of glass impingers and several optional procedures for the analysis of the collected material to arrive at the mass of particulate matter in the sample. The selection of different analyses options results in the creation of different levels of artifacts. Artifacts formed in the Method 202 impingers translates into a bias in the particulate matter emissions reported in the compliance test reports. These biases translate into biases in emissions factors. The use of biased emissions factors in turn produces biased national, regional and facility specific particulate matter emissions inventories reported in the NEI, SIPs, and periodic reports required by the CERR.

On November 1, 2005, EPA proposed a rule establishing minimum requirements for the preparation, adoption, and submittal of acceptable SIPs for fine particulate matter. Within the preamble of this proposed rule were discussions on requirements for emissions inventories, source test methods, and emissions reporting of primary particulate matter emissions. These discussions identified the need to report both the filterable particulate matter less than 2.5 $\mu$m in aerodynamic diameter and the condensable fraction of particulate matter emissions. Comments on the proposed rule highlighted imprecision and biases associated with applying the condensable test method, the lack of a method to size the filterable particulate matter, and the need for publishing test methods in the Federal Register.

In 2006, EPA assigned ERG a work assignment to generate information to characterize imprecision and bias in the existing PM2.5 NEI. Additionally, the 2006 work assignment developed information to identify methodologies to improve emissions factors used to generate emissions estimates in future inventories (NEI, SIPs, and data required by the CERR), and site-specific compliance test information. The 2006 work assignment also focused on developingadditional modifications that may further reduce Method 202 bias.

As part of the 2006 work, EPA solicited several external organizations to participate in the study of Method 202 artifact formation and reduction. The participation of these organizations ranged from reviewing and commenting on test plans to conducting independent laboratory evaluations to replicate EPA studies and to address separate issues of importance to a specific organization. Other tasks already assigned in this work assignment include: 1) developing a Quality Assurance Project Plan for a set of laboratory experiments, 2) coordinating external organization plans for supplementing the EPA laboratory experiments, 3) completion of the EPA conducted laboratory experiments, 4) assembling and analyzing the combined data, 5) documenting the results of all of the collected work and 6) preparing a test method for posting to the Emissions Measurement Center web site (www.epa.gov\ttn\emc).

EPA is changing this work assignment to:

1. Assist the WAM evaluate and effect technical and editorial changes to the test method recommended by stakeholders.
2. Assist the WAM prepare two draft Federal Register packages to propose or promulgate PM10 and PM2.5 source test methods in 40CFR51 Appendix M.
3. Prepare in draft form, a training course for educating individuals in the proper specification, application, and conduct of PM10 and PM2.5 source testing.

Revised Statement of Work

Task 1. The contractor shall update the approved work assignment plan as required by the contract. The contractor shall revise the approved work assignment plan as required to incorporate those additional tasks included in this work assignment change. The revised work assignment plan shall be an abbreviated plan with updated estimates of contractor resources and costs.

Task 2 through 6. No Change.

Task 7. The contractor shall provide periodic (approximately every two months) evaluations of stakeholder submitted recommendations for technical or editorial changes in the test method posted on the EMC web site. The contractor shall provide the WAM recommendations for incorporating those recommendations that simplify the test method, improve the precision of the test method, improve the quality assurance components of the method, clarify the requirements of the method or correct typographical errors.

Task 8. As requested by the WAM, the contractor shall recommend limited laboratory evaluations to assess the impact of stakeholder submitted recommendations for technical changes to the test method. Following approval by the WAM, the contractor shall conduct those limited laboratory evaluations. The contractor shall report to the WAM, the results of the laboratory evaluations and recommendations for revising the test method.

Task 9. The contractor shall prepare two draft Federal Register packages. One package will propose revisions to EPA Method 201A to include particulate

matter sizing at 2.5 uM as presented in Conditional Test Method 040, propose revisions to EPA Method 202 as presented in the final test method developed in this work assignment and propose a new EPA test method as presented in Conditional Test Method 039. The second Federal Register Package will be a direct final promulgation of the revisions of EPA Method 201A and 202.

Task 10. The contractor shall prepare in draft form, a training course for posting to the EMC web site that provides additional supporting information to individuals who will use these methods, oversee the conduct of these methods, specify the use of these test method, or need to understand the methods to perform their jobs. The contractor shall target those individuals in EPA, State and local agencies who write or review NSR/PSD and Title V permits, rules developers, enforcement officers, and compliance assessors. The contractor shall also target individuals external to government to include source test contractors, environmental managers of regulated entities, environmental consultants for regulated entities or State agencies.

Schedule of Additional Deliverables:

| Deliverable | Week of Contract | Estimated Date |
|---|---|---|
| Revised Contract plan and cost estimate. | 28 | April 20, 2007 |
| First evaluation of stakeholder recommended revisions. | 30 | May 4, 2007 |
| Draft outline and boilerplate of Federal Register preambles. | 31 | May 11, 2007 |
| First revision of test method for posting to the EMC web site. | 33 | May 25, 2007 |
| Draft Federal Register preambles. | 35 | June 8, 2007 |
| Second evaluation of stakeholder recommended revisions. | 37 | June 22, 2007 |
| Second revision of test method for posting to the EMC web site. | 40 | July 13, 2007 |
| Second Draft of Federal Register preambles. | 42 | July 27, 2007 |
| Third evaluation of stakeholder recommended revisions. | 44 | August 10, 2007 |
| Third revision of test method for posting to the EMC web site. | 48 | September 7, 2007 |
| Final Federal Register preambles with final revised test methods. | 52 | September 28, 2007 |

Draft Conditional Test Method 20X
March 19, 2007

# DRAFT METHOD 20X - THE DETERMINATION OF TOTAL PM10 AND PM2.5 PARTICULATE EMISSIONS (CONSTANT SAMPLING RATE PROCEDURES) FROM STATIONARY SOURCES

## 1. SCOPE AND APPLICABILITY

1.1 Scope

The U.S. Environmental Protection Agency (U.S. EPA or "we") developed this method to describe the procedures that the stack tester ("you") must follow to measure particulate matter emissions equal to or less than a nominal aerodynamic diameter of 10 microns (PM10) and 2.5 microns (PM2.5). This method includes procedures for both filterable (material that does not pass through a filter or a cyclone/filter combination) and condensable particulate matter (material that condenses after passing through a filter).

1.2 Applicability

You can use this method to measure both filterable and condensable stationary source emissions. Filterable particulate matter is measure with the in-stack portion of this method (i.e., materials that are solid or liquid at stack conditions). Condensable particulate matter is measured in the emissions after removal from the stack. You may use this method with only stationary sources.

1.3 Responsibility

You are responsible for obtaining the equipment and supplies you will need in this method. You must also develop your own procedures for following this method and any additional procedures to ensure accurate sampling and analytical measurements.

1.4 Results

To obtain reliable results, you must have a thorough knowledge of the following test methods:

(a) Method 2 of Appendix A to 40 CFR part 60 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube).

(b) Method 1 of Appendix A to 40 CFR part 60 - Sample and Velocity Traverses for Stationary Sources.

(c) Method 3 of Appendix A to 40 CFR part 60 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight.

(d) Method 4 of Appendix A to 40 CFR part 60 - Determination of Moisture Content in Stack Gases.

(e) Method 5 of Appendix A to 40 CFR part 60 - Determination of Particulate Emissions from Stationary Sources.

1.5 Additional Methods

We do not anticipate that you will need additional test methods to measure ambient source contributions because these contributions are insignificant for most of the sources using this test method. However, when an adjustment for the ambient air particulate matter is needed, use the ambient air reference methods to quantify the ambient air contribution. Particulate collected by the ambient air samplers that vaporize at the process temperature require additional adjustments.

1.6 Limitations

You can not use this method to measure emissions following a wet scrubber because this method is not applicable for in-stack gases containing water droplets. Stacks with entrained moisture droplets may have water droplets larger than the cut sizes for the cyclones and these water droplets normally contain particles that are PM10 and PM2.5. To measure PM10 and

PM2.5 in emissions where water droplets are known to exist, we recommend that you use Method 5 of Appendix A to 40 CFR part 60.

1.7 Conditions

You can use this method to obtain both particle sizing and total filterable particulate if the isokinetics are within 90-110 percent, the number of sampling points are the same as Method 17 of Appendix A to 40 CFR part 60 or Method 5 of Appendix A to 40 CFR part 60 requirements, and the in-stack filter temperature is within the acceptable range. The acceptable range for the in-stack filter temperature is generally defined as the typical range of temperature for emission gases. The acceptable range will vary depending on the source and control technology. To satisfy Method 5 criteria, you may need to remove the in-stack filter and use an out-of-stack filter and recover the probe between the PM2.5 particle sizer and the filter.

In addition, to satisfy Method 5 and Method 17 criteria, you may need to sample from more than 12 traverse points. The increased number of sampling points may require the use of multiple nozzles to maintain isokinetics between 90 and 110 percent and to maintain the minimum/maximum nozzle/stack velocity ratios within acceptable ranges. Be aware that this method determines in-stack PM10 and PM2.5 filterable emissions by sampling from a recommended maximum of 12 sample points, at a constant flow rate through the train (the constant flow is necessary to maintain the size cuts of the cyclones), and with a filter that is at the stack temperature. Method 17 or Method 5 trains are operated isokinetically with varying flow rates through the train. These methods sample from as many as 24 sample points. Method 5 uses an out-of-stack filter that is maintained at a constant temperature of 248°F. Further, to use this method in place of Method 17 or Method 5, you must extend the sampling time so that the

minimum mass that you can weigh is collected on each of the portions of this sampling train. Also, if you are using this method as an alternative to a required performance test, you must receive approval from the appropriate authorities prior to conducting the test.

## 2. SUMMARY OF METHOD

2.1 Summary

To measure PM10 and PM2.5, extract a sample of gas at a predetermined constant flow rate through an in-stack sizing device. The sizing device separates particles with nominal aerodynamic diameters of PM10 and PM2.5. To minimize variations in the isokinetic sampling conditions, you must establish well-defined limits. Once a sample is obtained, remove uncombined water from the particulate. Then use gravimetric analysis to determine the particulate mass for each size fraction.

This method combines filterable particulate procedures from Method 201A of Appendix M to 40 CFR part 51 with the PM2.5 cyclone from a conventional five-stage cascade cyclone train, plus condensable particulate recovery procedures adapted from Method 202 of Appendix M to 40 CFR part 51. Improvements to fine particulate measurement include the addition of a PM2.5 cyclone between the PM10 cyclone and the stack temperature filter of the sampling train defined by Method 201A. Without the addition of the PM2.5 cyclone, the filterable particulate portion of the sampling train used in this method is the same sampling train found in Method 201A. Improvements to condensable particulate measurement include addition of a water drop out and ambient filter after the in-stack filter. Figure 1 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method presents the schematic of the sampling train configured with these changes.

2.2 Condensable Particulate Matter

Condensable particulate matter (CPM) is collected in the impinger portion of the sampling train as described in this method. The impinger contents are immediately purged after the run with nitrogen ($N_2$) to remove dissolved sulfur dioxide ($SO_2$) gases from the impinger contents. The impinger solution is then extracted with methylene chloride ($MeCl_2$). The organic and aqueous fractions are then taken to dryness and the residues weighed. The total of both the aqueous and organic fractions represents the CPM.

2.3 Dry impinger and additional filter

The potential artifacts from $SO_2$ are reduced using a condenser and drop out impinger to separate CPM from reactive gases. No water is added to the impingers prior to the start of sampling. To improve the collection efficiency of CPM, an additional filter is placed between the second and third impinger.

## 3. DEFINITIONS

Use the following nomenclature:

| | | |
|---|---|---|
| A | = | Area of stack or duct at sampling location, square inches. |
| $A_n$ | = | Area of nozzle, square feet. |
| $b_f$ | = | Average blockage factor calculated in Equation 25, dimensionless. |
| $B_{ws}$ | = | Moisture content of gas stream, fraction (e.g., 10% $H_2O$ is $B_{ws}$ = 0.10). |
| C | = | Cunningham correction factor for particle diameter, $D_p$, and calculated using the actual stack gas temperature, dimensionless. |
| $\%CO_2$ | = | Carbon Dioxide content of gas stream, % by volume. |
| CPM | = | Condensable particulate matter |
| $C_a$ | = | Acetone blank concentration, mg/mg. |
| $C_{cpm}$ | = | Concentration of the condensable particulate matter in the stack gas, dry basis, corrected to standard conditions, g/dscf. |
| $C_{fPM10}$ | = | Conc. of filterable $PM_{10}$ particulate matter, gr/DSCF. |
| $C_{fPM2.5}$ | = | Conc. of filterable $PM_{2.5}$ particulate matter, gr/DSCF. |

$C_p$ = Pitot coefficient for the combined cyclone pitot, dimensionless.
$C_p'$ = Coefficient for the pitot used in the preliminary traverse, dimensionless.
$C_r$ = Re-estimated Cunningham correction factor for particle diameter equivalent to the actual cut size diameter and calculated using the actual stack gas temperature, dimensionless.
$C_{SO4}$ = Concentration of $SO_4^{-2}$ in the sample, mg/ml.
$C_{tf}$ = Conc. of total filterable particulate matter, gr/DSCF.
$C_1$ = -150.3162 (micropoise)
$C_2$ = 18.0614 (micropoise/$K^{0.5}$)
= 13.4622 (micropoise/$R^{0.5}$)
$C_3$ = 1.19183 x $10^6$ (micropoise/$K^2$)
= 3.86153 x $10^6$ (micropoise/$R^2$)
$C_4$ = 0.591123 (micropoise)
$C_5$ = 91.9723 (micropoise)
$C_6$ = 4.91705 x $10^{-5}$ (micropoise/$K^2$)
= 1.51761 x $10^{-5}$ (micropoise/$R^2$)
D = Inner diameter of sampling nozzle mounted on Cyclone I, in.
$D_p$ = Physical particle size, micrometers.
$D_{50}$ = Particle cut diameter, micrometers.
$D_{50-1}$ = Re-calculated particle cut diameters based on re-estimated $C_r$, micrometers.
$D_{50LL}$ = Cut diameter for cyclone I corresponding to the 2.25 micrometer cut diameter for cyclone IV, micrometers.
$D_{50N}$ = $D_{50}$ value for cyclone IV calculated during the Nth iterative step, micrometers.
$D_{50(N+1)}$ = $D_{50}$ value for cyclone IV calculated during the N+1 iterative step, micrometers.
$D_{50T}$ = Cyclone I cut diameter corresponding to the middle of the overlap zone shown in Figure 8 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method, micrometers.
I = Percent isokinetic sampling, dimensionless.
$K_p$ = 85.49, [(ft/sec)/(pounds/mole -°R)].
$m_a$ = Mass of residue of acetone after evaporation, mg.
$m_b$ = Sum of the mass of the water and $MeCl_2$ blanks, mg.
$m_c$ = Mass of the $NH_4^+$ added to sample to form ammonium sulfate, mg.
$m_i$ = Mass of inorganic CPM matter, mg.
$m_o$ = Mass of organic CPM, mg.
$m_r$ = Mass of dried sample from inorganic fraction, mg.
$M_d$ = Molecular weight of dry gas, pounds/pound mole.
$M_w$ = Molecular weight of wet gas, pounds/pound mole.
$M_1$ = Milligrams of particulate matter collected on the filter, $\leq$ 2.5 micrometers.

$M_2$ = Milligrams of particulate matter recovered from Container #2 (acetone blank corrected), >10 micrometers.

$M_3$ = Milligrams of particulate matter recovered from Container #3 (acetone blank corrected), ≤10 and >2.5 micrometers.

$M_4$ = Milligrams of particulate matter recovered from Container #4 (acetone blank corrected), ≤2.5 micrometers.

N = Normality of the $NH_4OH$, mg/ml.

$N_{tp}$ = Number of iterative steps or total traverse points.

$N_{re}$ = Reynolds number, dimensionless.

$\%O_{2,wet}$ = Oxygen content of gas stream, % by volume of wet gas. [**Note:** The oxygen percentage used in Equation 3 is on a *wet* gas basis. That means that since oxygen is typically measured on a dry gas basis, the measured $\%O_2$ must be multiplied by the quantity $(1 - B_{ws})$ to convert to the actual volume fraction. Therefore, $\%O_{2,wet} = (1 - B_{ws}) * \%O_{2dry}$ ]

$P_{bar}$ = Barometric pressure, in. Hg.

$P_s$ = Absolute stack gas pressure, in. Hg.

$Q_s$ = Sampling rate for cyclone I to achieve specified $D_{50}$, ACFM.

$Q_{sST}$ = Dry gas sampling rate through the sampling assembly, DSCFM.

$Q_I$ = Sampling rate for cyclone I to achieve specified $D_{50}$, ACFM.

$Q_{IV}$ = Sampling rate for cyclone IV to achieve specified $D_{50}$, ACFM.

$R_{max}$ = Nozzle/stack velocity ratio parameter, dimensionless.

$R_{min}$ = Nozzle/stack velocity ratio parameter, dimensionless.

$T_m$ = Meter box and orifice gas temperature, °R.

$t_n$ = Sampling time at point n, min.

$t_r$ = Total projected run time, min.

$T_s$ = Absolute stack gas temperature, °R.

$t_1$ = Sampling time at point 1, min.

$v_{max}$ = Maximum gas velocity calculated from Equations 18 or 19, ft/sec.

$v_{min}$ = Minimum gas velocity calculated from Equations 16 or 17, ft/sec.

$v_n$ = Sample gas velocity in the nozzle, ft/sec.

$v_s$ = Velocity of stack gas, ft/sec.

$V_a$ = Volume of acetone blank, mL.

$V_{aw}$ = Volume of acetone used in blank wash, mL.

$V_c$ = Quantity of water captured in impingers and silica gel, mL.

$V_m$ = Dry gas meter volume sampled, ACF.

$V_{ms}$ = Dry gas meter volume sampled, corrected to standard conditions, DSCF.

$V_{ws}$ = Volume of water vapor, SCF.

$V_b$ = Volume of aliquot taken for IC analysis, ml.

$V_{ic}$ = Volume of impinger contents sample, ml.

$W_a$ = Weight of residue in acetone blank wash, mg.

Z = Ratio between estimated cyclone IV $D_{50}$ values, dimensionless.

| | | |
|---|---|---|
| $^{a}H$ | = | Meter box orifice pressure drop, in. W.C. |
| $^{a}H_{@}$ | = | Pressure drop across orifice at flow rate of 0.75 SCFM at standard conditions, in. W.C. [**Note:** specific to each orifice and meter box] |
| $[(^{a}p)^{0.5}]_{avg}$ | = | Average of square roots of the velocity pressures measured during the preliminary traverse, in. W.C. |
| $^{a}p_{m}$ | = | Observed velocity pressure using S-type pitot tube in preliminary traverse, in. W.C. |
| $^{a}p_{max}$ | = | Maximum velocity pressure, in. W.C. |
| $^{a}p_{min}$ | = | Minimum velocity pressure, in. W.C. |
| $^{a}p_{n}$ | = | Velocity pressure measured at point n during the test run, in. W.C. |
| $^{a}p_{s}$ | = | Velocity pressure calculated in Equation 24, in. W.C. |
| $^{a}p_{s1}$ | = | Velocity pressure adjusted for combined cyclone pitot tube, in. W.C. |
| $^{a}p_{s2}$ | = | Velocity pressure corrected for blockage, in. W.C. |
| $^{a}p_{1}$ | = | Velocity pressure measured at point 1, in. W.C. |
| $V_{t}$ | = | Volume of $NH_4OH$ titrant, ml. |
| g | = | Dry gas meter gamma value, dimensionless. |
| µ | = | Gas viscosity, micropoise. |
| ⊗ | = | Total run time, minutes. |
| $\oplus_{a}$ | = | Density of acetone, mg/mL (see label on bottle). |
| 12.0 | = | Constant calculated as 60% of 20.5 square inch cross-sectional area of combined cyclone head, square inches. |

## 4. INTERFERENCES /LIMITATIONS

4.1 Ammonia

In sources that use ammonia injection as a control technique for hydrogen chloride (HCl) or nitrogen oxides ($NO_x$), ammonium salts are measured as CPM. The inorganic fraction should be taken to near dryness (less than 1 ml liquid) in the oven and then allowed to air dry at ambient temperature to prevent ammonium chloride ($NH_4Cl$) from vaporizing.

## 5. SAFETY

Disclaimer. You may have to use hazardous materials, operations, and equipment while performing this method. We do not provide information on appropriate safety and health

practices. You are responsible for determining the applicability of regulatory limitations and establishing appropriate safety and health practices. Handle materials and equipment properly.

## 6. EQUIPMENT AND SUPPLIES

Figure 2 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method shows details of the combined cyclone heads used in this method. The filterable particulate portion of the sampling train is the same sampling train described in Method 17 of Appendix A of 40 CFR part 60 with the exception of the PM10 and PM2.5 sizing devices and in-stack filter. The equipment used in the CPM portion of the train is a combination of hardware and glassware used in Method 23 and Method 202 of Appendix A of 40 CFR part 60. The following paragraphs describe the sampling train's primary design features in detail.

6.1 Filterable Particulate Sampling Train Components

6.1.1 Nozzle. You must use nozzles that are stainless steel (316 or equivalent) or Teflon®-coated stainless steel with a sharp tapered leading edge. We recommend that you choose one of the 12 nozzles listed in Figure 3 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method because they meet design specifications. However, if you don't choose a nozzle from this list, then you must choose a nozzle that meets the criteria in paragraph 5.2 of EPA Method 201A of Appendix M to 40 CFR part 51. We also recommend that you have a large number of nozzles in small diameter increments available to increase the likelihood of using a single nozzle for the entire traverse.

6.1.2 PM10 and PM2.5 sizer. Choose a stainless steel (316 or equivalent) PM10 and PM2.5 sizer. The sizing devices must be cyclones that meet the design

specifications shown in Figures 3, 4, and 5 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method. Use a caliper to verify the dimensions of the PM10 and PM2.5 sizers to within ±0.02 cm of the design specifications. Example suppliers of PM10 and PM2.5 sizers include the following:

(a) Environmental Supply Company, Inc.
2142 Geer Street
Durham, North Carolina 27704
(919) 956-9688
(919) 682-0333 (fax)

(b) Apex Instruments
P.O. Box 727
125 Quantum Street
Holly Springs, North Carolina 27540
(919) 557-7300
(919) 557-7110 (fax)

(c) Andersen Instruments Inc.
500 Technology Court
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (fax)

6.1.3 Filter holder. You must use a filter holder that is either stainless steel (316 or equivalent) or Teflon®-coated stainless steel. Commercial size filter holders are available depending upon project requirements. You should be able to find a commercial filter holder to support 25-mm, 47-mm, and 63-mm diameter filters. Commercial size filter holders contain a Teflon® O-ring, stainless steel screen that supports the filter, and a final Teflon® O-ring. Screw the assembly together and attach to the outlet of cyclone IV.

6.1.4 Pitot tube. You must use a pitot tube made of heat resistant tubing. Attach the pitot tube to the probe with stainless steel fittings. Follow the specifications for the pitot tube and its orientation to the inlet nozzle given in paragraph 6.1.1.3 of Method 5 of Appendix A to 40 CFR part 60.

6.1.5 Probe liner. The probe extension must be glass-lined or Teflon®. Follow the specifications in paragraph 6.1.1.2 of Method 5 of Appendix A to 40 CFR part 60.

6.1.6 Differential pressure gauge, condensers, metering systems, barometer, and gas density determination equipment. Follow the requirements in paragraphs 6.1.1.4 through 6.1.3 of Method 5 of Appendix A to 40 CFR part 60, as applicable.

6.2 Condensable Particulate Sampling Train Components

6.2.1 Condenser. The following components must be used: A Method 23 condenser as described in section 2.1.2 of Method 23 of Appendix A to 40 CFR part 60, followed by a knockout impinger or flask, followed by a modified Greenburg-Smith design with an open tube tip as described in section 6.1.1.8 of Method 5 of Appendix A to 40 CFR part 60.

6.2.2 Ambient Temperature Filter holder. You must use a filter holder that is either glass, stainless steel (316 or equivalent), or Teflon®-coated stainless steel. Commercial size filter holders are available depending upon project requirements. You should be able to find a commercial filter holder to support 25 mm, 47 mm, 63 mm, and 110 mm diameter filters. Commercial size filter

holders contain a Teflon® O-ring, stainless steel, ceramic or Teflon® filter support and a final Teflon® O-ring.

6.3 Sample Recovery Equipment

6.3.1 Filterable Particulate Recovery. You will need the following equipment to quantitatively determine the amount of filterable particulate matter recovered from the sampling train. Follow the requirements specified in paragraphs 6.2.1 through 6.2.8 of Method 5 of Appendix A to 40 CFR part 60, respectively.

(a) Filter holder brushes

(b) Wash bottles

(c) Glass sample storage containers

(d) Petri dishes

(e) Graduated cylinders and balance

(f) Plastic storage containers

(g) Funnel

(h) Rubber policeman

6.3.2 Condensable Particulate Matter Recovery

6.3.2.1 *$N_2$ Purge Line*. Inert tubing and fittings capable of delivering 0 to 28 liters/min of $N_2$ gas to the impinger train from a standard gas cylinder (see Figure 202-2). Standard 0.95 cm (3/8-inch) plastic tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

6.3.2.2 *Rotameter*. Capable of measuring gas flow at 20 liters/min.

6.3.2.3 *UHP Nitrogen Gas*. Compressed ultrapure nitrogen, regulator and filter to provide up to 20 liters/min purge gas for 1 hour through the sampling train.

6.3.3 Analysis. The following equipment is necessary for CPM sample recovery and analysis:

Separatory Funnel. Glass, 1-liter.

Weighing Tins. 50 to 350-ml.

Drying Equipment. Hot plate and oven with temperature control.

Pipets. 5-ml.

Burette. Glass, 0 to 100 mL in 1.0 mL graduation

Glassware Cleaning. All sampling train glassware must be cleaned prior to the test with soap and tap water, water, and rinsed using tap water, water, acetone, and finally, methylene chloride. It is important to completely remove all silicone grease from areas that will be exposed to the methylene chloride during sample recovery.

## 7. REAGENTS AND STANDARDS

7.1 Sample Collection

To collect a sample, you will need a filter and silica gel. You must also have water and crushed ice. You will find additional information on each of these items in the following summaries.

7.1.1 Filter. You must use a glass fiber, quartz, or Teflon® filter that does not a have an organic binder. The filter must also have an efficiency of at least 99.95 percent

(<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. Conduct the filter efficiency test in accordance with ASTM Method D2986-71, 78, 95a (incorporated by reference). Alternatively, you may use test data from the supplier's quality control program. If the source you are sampling has $SO_2$ or $SO_3$ emissions, you must use a filter that will not react to $SO_2$ or $SO_3$. Depending on your application and project data quality objectives (DQOs), filters are commercially available in 25-mm, 47-mm, 63-mm, and 110-mm sizes.

7.1.2 Silica gel. You must choose an indicating-type silica gel of 6 to 16 mesh. We must approve other types of desiccants (equivalent or better) before you use them. Allow the silica gel to dry for 2 hours at 175°C (350°F) if it is being reused. You do not have to dry new silica gel.

7.1.3 Water. Use deionized distilled water (to conform to ASTM D 1193-77, 91 Type 3) to recover material caught in the impinger, if required. If you use water to recover this material, then you must run blanks before you begin your testing. Running blanks before field use will verify low blank concentrations, thereby reducing the potential for a high field blank on test samples.

7.1.4 Crushed ice. Obtain this from the best readily available source.

7.2 Reagents for Sample Recovery

7.2.1 Acetone. You must use acetone that is stored in glass bottles. Do not use acetone from metal containers because it normally produces a high residue blank. You must use acetone with blank values < 1 ppm, by weight residue. You may run acetone blanks prior to field use to confirm low blank values.

In no case shall a blank value of greater than 1E-06 of the weight of acetone used in sample recovery be subtracted from the sample weight.

7.2.2 Methylene Chloride, ACS grade. Run blanks prior to use and use only methylene chloride with low blank values (0.001 percent). You must use methylene chloride with a blank value <1.5 ppm, by weight, residue. In no case shall a blank value of greater than 1.6E-06 of the weight of methylene chloride used in sample recovery and extraction be subtracted from the sample weight.

7.2.3 Water. Use deionized distilled water to conform to the same specifications as section 7.1.3 of this method.

7.3 Reagents for Sample Analysis

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade. You will need acetone, methylene chloride, and anhydrous sodium sulfate for the sample analysis.

7.3.1 Methylene Chloride. Run blanks prior to use and use only methylene chloride with low blank values (0.001 percent). Methylene chloride with a blank value <1.5 ppm, by weight, residue. In no case shall a blank value of greater than 1.6E-06 of the weight of methylene chloride used in sample recovery and extraction be subtracted from the sample weight.

7.3.3 Organic Extract Desiccant. Use indicating-type anhydrous sodium sulfate.

7.3.4 Ammonium Hydroxide. NIST traceable or equivalent (0.1 N) $NH_4OH$.

7.3.3 Water. Use deionized distilled water (to conform to ASTM D 1193-77, 91 Type 3) to recover material caught in the impinger, if required. If you use water to recover this material, then you must run blanks before you begin testing. Running blanks before field use will verify low blank concentrations, thereby reducing the potential for a high field blank on test samples.

7.3.4 Phenolphthalein. The pH indicator solution, 0.05 percent in 50 percent alcohol.

## 8. SAMPLE COLLECTION, PRESERVATION, STORAGE, AND TRANSPORT

8.1 Qualifications

This is a complex test method. To obtain reliable results, you must be trained and experienced with in-stack filtration systems (such as, cyclones, impactors, and thimbles) and their operations.

8.2 Preparations

Follow the pretest preparation instructions in paragraph 8.1 of Method 5 of Appendix A to 40 CFR part 60.

8.3 Site Setup

You must perform the following items to properly set up for this test:

(a) Determine the sampling site location and traverse points.

(b) Calculate probe/cyclone blockage.

(c) Verify the absence of cyclonic flow.

(d) Complete a preliminary velocity profile and select a nozzle(s).

8.3.1 Sampling site location and traverse point determination. Follow the standard procedures in Method 1 of Appendix A to 40 CFR part 60 to select the appropriate sampling site. Then do all of the following:

(a) Sampling site. Choose a location that maximizes the distance from upstream and downstream flow disturbances.

(b) Traverse points. The recommended maximum number of traverse points at any location is 12 and shown in Figure 6 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method. Prevent the disturbance and capture of any solids accumulated on the inner wall surfaces by maintaining a 1 inch distance from the stack wall (½ inch for sampling locations less than 24 inches in diameter).

(c) Round or rectangular duct or stack. If a duct or stack is round with two ports located 90° apart, use six sampling points on each diameter. Use a 3x4 sampling point layout for rectangular ducts or stacks. Consult with the Administrator to receive approval for other layouts before you use them.

(d) Sampling ports. You may need new sampling ports in most of the sampling port locations installed for sampling by Method 5 of Appendix A to 40 CFR part 60 or Method 17 of Appendix A to 40 CFR part 60 for total filterable particulate sampling. When you must use nozzles smaller than 0.16 inch in diameter, the sampling port diameter must be 6 inches. Do not use the conventional 4 inch diameter port because it will not support the length of the nozzle extending from the PM10 cyclone. [**Note:** If the port

nipple is short, you may be able to "hook" the sampling head through a smaller port into the duct or stack.]

8.3.2 Probe/cyclone blockage calculations. Follow the procedures in the next two paragraphs, as appropriate.

8.3.2.1 *Ducts with diameters greater than 24 inches.* Minimize the blockage effects of the combination of the in-stack nozzle/cyclones and filter assembly for ducts with diameters greater than 24 inches by keeping the cross-sectional area of the assembly at 3 percent or less of the cross-sectional area of the duct.

8.3.2.2 *Ducts with diameters between 24 and 18 inches.* Ducts with diameters between 24 inches to 18 inches have blockage effects ranging from 3 percent to 6 percent, as illustrated in Figure 7 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method. Therefore, when you conduct tests on these small ducts, you must adjust the observed velocity pressures for the estimated blockage factor whenever the combined sampling apparatus blocks more than 3 percent of the stack or duct (see paragraphs 8.7.2.2 and 8.7.2.3 of this section on the probe blockage factor and the final adjusted velocity pressure, respectively).

8.3.3 Cyclonic flow. Do not use the combined cyclone sampling head at sampling locations subject to cyclonic flow. Also, you must follow Method 2 procedures to determine the presence or absence of cyclonic flow. Then perform the

following calculations. [**Note:** You can minimize cyclonic flow conditions by placing gas flow straighteners upstream of the sampling location.]

(a) Find the angle that has a null velocity pressure. Insert the S-type pitot tube at each of the traverse points and rotate until you locate the angle that has a null velocity pressure.

(b) Determining a sampling location. Average the absolute values of the angles that have a null velocity pressure. Do not use the sampling location if the average absolute value exceeds 20°.

8.3.4 Preliminary velocity profile. Conduct a preliminary Method 2 of Appendix A to 40 CFR part 60 velocity traverse, as well as the measurements below. The purpose of the velocity profile is to determine all of the following:

(a) The gas sampling rate for the combined probe/cyclone sampling head.

(b) The appropriate nozzle(s) to maintain the required velocity pressure range and isokinetic range.

(c) The necessary sampling duration to obtain sufficient particulate catch weights.

8.3.4.1 *Preliminary traverse.* You must use an S-type pitot tube with a conventional thermocouple to conduct the traverse. Conduct the preliminary traverse as close as possible to the anticipated testing time on sources that are subject to hour-by-hour gas flow rate variations of approximately ±20% and/or gas temperature variations of approximately ±50°F. Follow the following instructions. [**Note:** You

should be aware that these variations can cause errors in the cyclone cut diameters and the isokinetic sampling velocities.]

8.3.4.2 *Velocity pressure range*. Insert the S-type pitot tube at each traverse point and record the range of velocity pressures measured on the Method 2 of Appendix A to 40 CFR part 60 data form. You will use this later to select the appropriate nozzle(s).

8.3.4.3 *Initial gas stream viscosity and molecular weight*. Determine the average gas temperature, average gas oxygen content, average carbon dioxide content, and estimated moisture content. You will use this information to calculate the initial gas stream viscosity (Equation 3) and molecular weight (Equations 1 and 2). [**Note:** You must follow the instructions outlined in Method 4 to estimate the moisture content. You may use a wet bulb-dry bulb measurement or hand-held hygrometer measurement to estimate the moisture content of sources with gas temperatures less than 160°F.]

8.3.4.4 *Particulate matter concentration in the gas stream*. Determine the particulate matter concentration in the gas stream through qualitative measurements or estimates. Having an idea of what the particulate concentration is in the gas stream is not essential but will help you determine the appropriate sampling time to acquire sufficient particulate matter weight for better accuracy at the source emission level. The collectable particulate matter weight requirements depend

primarily on the types of chemical analyses needed to characterize the emissions. Estimate the collectable particulate matter concentrations in the >10 micrometer, 10 and >2.5 micrometers, and 2.5 micrometer size ranges.

8.4 Pre-test Calculations

You must perform pre-test calculations to help select the appropriate gas sampling rate through cyclone I (PM10) and cyclone IV (PM2.5). Choosing the appropriate sampling rate will allow you to maintain the appropriate particle cut diameters based upon preliminary gas stream measurements, as specified in Table 2 of the Tables, Diagrams, Flowcharts, and Validation Data in section 17 of this method.

8.4.1 Gas sampling rate. The gas sampling rate is defined by the performance curves for both cyclones, as illustrated in Figure 8 of the Tables, Diagrams, Flowcharts, and Validation Data in section 17 of this method. You must use the calculations in paragraph 8.5 of this section to achieve the appropriate cut size specification for each cyclone. The optimum gas sampling rate is the overlap zone defined as the range below the cyclone IV 2.25 micrometer curve down to the cyclone I 11.0 micrometer curve (area between the two dark, solid lines in Figure 8 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method).

8.4.2 Choosing the appropriate sampling rate. You must select a gas sampling rate in the middle of the overlap zone (discussed in paragraph 8.4.1 of this section), as illustrated in Figure 8 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method to maximize the acceptable tolerance for slight variations

in flow characteristics at the sampling location. The overlap zone is also a weak function of the gas composition. [**Note:** You should be aware that the acceptable range is limited, especially for gas streams with temperatures less than approximately 100°F.]

8.5 Test Calculations

You must perform all of the calculations in Table 1 of this paragraph, and the calculations described in paragraphs 8.5.1 through 8.5.5 of this section.

Table 1. Pretest Calculations

| If you are using... | To calculate... | Then use... |
|---|---|---|
| Prelimina ry data | dry gas molecular weight, $M_d$ | Equation 1 |
| Dry gas molecular weight ($M_d$) and preliminary moisture content of the gas stream | wet gas molecular weight, $M_W$ | Equation 2[a] |
| Stack gas temperature, and oxygen and moisture content of the gas stream | gas viscosity,μ | Equation 3 |
| Gas viscosity,μ | Cunningham correction factor[b], C | Equation 4 |
| Reynolds Number[c] ($N_{re}$) $N_{re} < 3162$ | preliminary lower limit cut diameter for cyclone I, $D_{50LL}$ | Equation 5 |
| $D_{50LL}$ from Equation 5 | cut diameter for cyclone I for middle of the overlap zone, $D_{50T}$ | Equation 6 |
| $D_{50T}$ from Equation 6 | final sampling rate for cyclone I, $Q_I(Q_s)$ | Equation 7 |
| $Q_I(Q_s)$ from Equation 7 | (verify) the assumed Reynolds number | Equation 8 |

[a] Use Method 4 of Appendix A to 40 CFR part 60 to determine the moisture content of the stack gas. Use a wet bulb-dry bulb measurement device or hand-held hygrometer to estimate moisture content of sources with gas temperature less than 160°F.

[b] For the lower cut diameter of cyclone IV, 2.25 micrometer.

[c] Verify the assumed Reynolds number using the procedure in paragraph 8.5.1, below, before proceeding to Equation 9.

8.5.1 The assumed Reynolds number. Verify the assumed Reynolds number ($N_{re}$) by substituting the sampling rate ($Q_s$) calculated in Equation 7 into Equation 8. Then use Table 2 of this paragraph to determine if the $N_{re}$ used in Equation 5 was correct.

Table 2. Verification of the Assumed Reynolds Number

| If the $N_{re}$ is ... | Then ... | And ... |
|---|---|---|
| < 3162 | Calculate DH for the meter box | |
| ≥ 3162 | Recalculate $D_{50LL}$ using Equation 10 | Substitute the "new" $D_{50LL}$ into Equation 6 to recalculate $D_{50T}$ |

8.5.2 Final sampling rate. You must recalculate the final sampling rate ($Q_s$) if the assumed Reynold's number used in your initial calculation is not correct. Use Equation 7 to recalculate the optimum sampling rate ($Q_s$).

8.5.3 Meter box DH. Use Equation 9 to calculate the meter box DH after you calculate the optimum sampling rate and confirm the Reynolds number. [**Note:** The stack gas temperature may vary during the test which could affect the sampling rate. If

this occurs, you must make slight adjustments in the meter box DH to maintain the correct constant cut diameters. Therefore, use Equation 9 to recalculate the DH values for 50°F above and below the stack temperature measured during the preliminary traverse (see paragraph 8.3.4.1) and document this information in the Tables, Diagrams, Flowcharts, and Validation Data section of this method under Table 3.]

8.5.4 Choosing a sampling nozzle. You must select one or more nozzle sizes to provide for near isokinetic sampling rate (that is, 80% to 120%). This will also minimize an isokinetic sampling error for the 10 micrometer particles at each point. First calculate the mean stack gas velocity, $v_s$, using Equation 11. Look at paragraph 8.7.2 for information on correcting for blockage and use of different pitot tube coefficients. Then use Equation 12 to calculate the diameter of a nozzle that provides for isokinetic sampling at the mean stack gas velocity at flow $Q_s$. From the available nozzles just smaller and just larger of this diameter, D, select the most promising nozzle(s). Perform the following steps for the selected nozzle(s).

8.5.4.1 *Minimum/maximum nozzle/stack velocity ratio*. Use Equation 14 to calculate the minimum nozzle/stack velocity ratio, $R_{min}$. Use Equation 15 to calculate the maximum nozzle/stack velocity ratio, $R_{max}$.

8.5.4.2 *Minimum gas velocity*. Use Equation 16 to calculate the minimum gas velocity ($v_{min}$) if $R_{min}$ is an imaginary number (negative value under the

square root function) or if $R_{min}$ is less than 0.5. Use Equation 17 to calculate $v_{min}$ if $R_{min}$ is greater than or equal to 0.5.

8.5.4.3 *Maximum stack velocity*. Use Equation 18 to calculate the maximum stack velocity ($v_{max}$) if $R_{max}$ is less than 1.5. Use Equation 19 to calculate the stack velocity if $R_{max}$ is greater than or equal to 1.5.

8.5.4.4 *Conversion of gas velocities to velocity pressure.* Use Equation 20 to convert $v_{min}$ to minimum velocity pressure, $\Delta p_{min}$. Use Equation 21 to convert $v_{max}$ to maximum velocity pressure, $\Delta p_{max}$.

8.5.4.5 Compare minimum and maximum velocity pressures with the observed velocity pressures at all traverse points during the preliminary test (see paragraph 3.4.2 of this section).

8.5.5 Optimum sampling nozzle. The nozzle you selected is appropriate if all the observed velocity pressures during the preliminary test fall within the range of the $\Delta p_{min}$ and $\Delta p_{max}$. Make sure the following requirements are met. Then follow the procedures in paragraphs 8.5.5.1 and 8.5.5.2.

(a) Choose an optimum nozzle that provides for isokinetic sampling conditions as close to 100% as possible. This is prudent because even if there are slight variations in the gas flow rate, gas temperature, or gas composition during the actual test, you have the maximum assurance of satisfying the isokinetic criteria. Generally, one of the two candidate nozzles selected will be closer to optimum (see paragraph 8.5.4).

(b) When testing is for PM2.5 only, you can have only two traverse points that are outside the range of the Dpmin and Dpmax. If the coarse fraction for PM10 determination is included, only one traverse point can fall outside the minimum-maximum velocity pressure range. However, you can select two or more nozzles so that the traverse points will be within the criteria calculated for each nozzle.

8.5.5.1 *Precheck*. Visually check the selected nozzle for dents before use.

8.5.5.2 *Attach the pre-selected nozzle*. Screw the pre-selected nozzle onto the main body of cyclone I using Teflon® tape. Use a union and cascade adaptor to connect the cyclone IV inlet to the outlet of cyclone I (see Figure 2 of the Tables, Diagrams, Flowcharts, and Validation Data of section 17 of this method).

8.6 Sampling Train Preparation

A schematic of the sampling train used in this method is shown in Figure 1 in Tables, Diagrams, Flowcharts, and Validation Data in section 17 of this method. The sampling train components and operation and maintenance are very similar to Method CTM 040 and Method 202. First, you must assemble the train and complete the leak check on the combined cyclone sampling head and pitot tube. Use the following procedures to prepare the sampling train. [**Note:** Do not contaminate the sampling train during preparation and assembly. You must keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.]

8.6.1 Sampling head and pitot tube. Assemble the combined cyclone train. The O-rings used in the train have a temperature limit of approximately 400°F. However, Teflon® O-rings can withstand 600°F without sealing problems. You must use cyclones with stainless steel sealing rings when stack temperatures exceed 600°F. You must also keep the nozzle covered to protect it from nicks and scratches.

8.6.2 Filterable particulate filter holder and pitot tube. Attach the pre-selected filter holder to the end of the combined cyclone sampling head (see Figure 2 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method). Attach the S-type pitot tube to the combined cyclones after the sampling head is fully attached to the end of the probe. [**Note:** The pitot tube tip must be mounted (1) slightly beyond the combined head cyclone sampling assembly and (2) at least one inch off the gas flow path into the cyclone nozzle. This is similar to the pitot tube placement in Method 17 of Appendix A to 40 CFR part 60.] Weld the sensing lines to the outside of the probe to ensure proper alignment of the pitot tube. Provide unions on the sensing lines so that you can connect and disconnect the S-type pitot tube tips from the combined cyclone sampling head before and after each run. [**Note:** Calibrate the pitot tube on the sampling head because the cyclone body is a potential source of interference. ]

8.6.3 Filter . You must number and tare the filters before use. To tare filters, desiccate each filters at 20 ± 5.6°C (68 ± l0°F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., <0.5 mg

change from previous weighing; record results to the nearest 0.l mg. During each weighing the filter must not be exposed to the laboratory atmosphere for longer than 2 minutes and a relative humidity above 50 percent. Alternatively , the filters may be oven-dried at l04°C (220°F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Use tweezers or clean disposable surgical gloves to place a labeled (identified) and pre-weighed filter in both filterable and condensable particulate filter holders. You must center the filter and properly place the gasket so that the sample gas stream will not circumvent the filter. Check the filter for tears after the assembly is completed. Then screw the filter housing together to prevent the seal from leaking.

8.6.4 Condenser. Add a condenser and a condensate drop out impinger without bubbler tube after the heated filter assembly. A Method 23 type stack gas condenser has been found adequate for this purpose. It must be capable of cooling the stack gas to less than 30°C (85°F).

8.6.5 Ambient Impinger. The drop out impinger is followed by a modified Greenburg Smith Impinger with no taper.(Figure 17.1). The drop out and impinger are placed in an insulated box with water at 80 to 85°F (25 to 30°C). At the start of the tests, the water drop out and impingers will be clean, without any water or reagent added.

8.6.6 Ambient Filter: A filter meeting the requirements in section 6.1.3 follows the Ambient Impinger.

8.6.7 Moisture Trap: An empty modified Greenburg Smith Impinger followed by an impinger containing silica gel is required or alternatives described in Method 5 be used to collect moisture that passes through the ambient filter.

8.6.8 Leak check. Use the procedures outlined in paragraph 8.4 of Method 5 of Appendix A to 40 CFR part 60 to leak check the entire sampling system. Specifically perform the following procedures:

8.6.8.1 *Sampling train*. You must pretest the entire sampling train for leaks. The pretest leak check must have a leak rate of not more than 0.02 ACFM or 4% of the average sample flow during the test run, whichever is less. Additionally, you must conduct the leak check at a vacuum equal to or greater than the vacuum anticipated during the test run. Enter the leak check results on the field test data sheet for the specific test. [**Note:** Do not conduct a leak check during port changes.]

8.6.8.2 *Pitot tube assembly*. After you leak check the sample train, you must perform a leak check of the pitot tube assembly. Follow the procedures outlined in section 8.4.1 of Method 5 of Appendix A to 40 CFR part 60.

8.6.9 Sampling head. You must preheat the combined sampling head to the stack temperature of the gas stream at the test location (± 10°C). This will heat the sampling head and prevent moisture from condensing from the sample gas stream. Record the site barometric pressure and stack pressure on the field test data sheet.

8.6.9.1 *Unsaturated stacks*. You must complete a passive warmup (of 30-40 min) within the stack before the run begins to avoid internal condensation. [**Note:** Unsaturated stacks do not have entrained droplets and operate at temperatures above the local dew point of the stack gas.]

8.6.9.2 *Shortened warm-up of unsaturated stacks*. You can shorten the warmup time by unthermostated heating outside the stack (such as by a heat gun). Then place the heated sampling head inside the stack and allow the temperature to equilibrate.

8.6.9.3 *Ambient Temperature drop out and impinger*. Ambient temperature water is added to the first impinger section/box. Water should be heated or cooled to maintain 80±5°F (30±3°C).

8.7 Sampling Train Operation

Operate the sampling train the same as described in section 4.1.5 of Method 5 of Appendix A to 40 CFR part 60, except use the procedures in this section of this method for isokinetic sampling and flow rate adjustment. Maintain the flow rate calculated in section 8.4.1 of this method throughout the run, provided the stack temperature is within 28°C (50°F) of the temperature used to calculate H. If stack temperatures vary by more than 28°C (50°F), use the appropriate H value calculated in section 8.5.3 of this method. Determine the minimum number of traverse points as in Figure 6. We recommend you round the number of minutes sampled at each point to the nearest 15 seconds. Perform the following procedures:

8.7.1 Sample point dwell time. You must calculate the dwell time (that is, sampling time) for each sampling point to ensure that the overall run provides a velocity-

weighted average that is representative of the entire gas stream. Vary the dwell time, or sampling time, at each traverse point proportionately with the point velocity.

8.7.1.1 *Dwell time at first sampling point.* Calculate the dwell time for the first point, $t_1$, using Equation 22. You must use the data from the preliminary traverse. Here, $N_{tp}$ equals the total number of traverse points.

8.7.1.2 *Dwell time at remaining sampling points.* Calculate the dwell time at each of the remaining traverse points, $t_n$, using Equation 23. This time you must use the actual test run data. [**Note:** Round the dwell times to 1/4 minutes.] Each traverse point must have a dwell time of at least two minutes.

8.7.2 Adjusted velocity pressure. When selecting your sampling points using your preliminary velocity traverse data, your preliminary velocity pressures must be adjusted to take into account the increase in velocity due to blockage. Also, you must adjust your preliminary velocity data for differences in pitot tube coefficients. Use the following instructions to adjust the preliminary velocity pressure.

8.7.2.1 *Different pitot tube coefficient.* You must use Equation 24 to correct the recorded preliminary velocity pressures if the pitot tube mounted on the combined cyclone sampling head has a different pitot tube coefficient

than the pitot tube used during the preliminary velocity traverse (see paragraph 8.3.4 of this method).

8.7.2.2 *Probe blockage factor*. You must use Equation 25 to calculate an average probe blockage correction factor ($b_f$) if the diameter of your stack or duct is between 18 and 24 inches. A probe blockage factor is calculated because of the flow blockage caused by the relatively large cross-sectional area of the combined cyclone sampling head, as discussed in paragraph 8.3.2.2 of this method and illustrated in Figure 7 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method. [**Note:** The sampling head (including the filter holder) has a projected area of approximately 20.5 square inches when oriented into the gas stream. As the probe is moved from the most outer to the most inner point, the amount of blockage that actually occurs ranges from approximately 4 square inches to the full 20.5 inches. The average cross-sectional area blocked is 12 square inches.]

8.7.2.3 *Final adjusted velocity pressure*. Calculate the final adjusted velocity pressure( $p_{s2}$) using Equation 26. [**Note:** Figure 7 of the Tables, Diagrams, Flowcharts, and Validation Data section of this method illustrates that the blockage effect of the large combined cyclone sampling head increases rapidly below diameters of 18 inches. Therefore, you must follow the procedures outlined in Method 1A to conduct tests in small stacks (<18 inches diameter). You must conduct

the velocity traverse downstream of the sampling location or immediately before the test run.]

8.7.3 Sample Collection. Collect samples the same as described in section 4.1.5 of Method 5 of Appendix A to 40 CFR part 60, except use the procedures in this section of this method for isokinetic sampling and flow rate adjustment. Maintain the flow rate calculated in section 8.5 of this method throughout the run, provided the stack temperature is within 28°C (50°F) of the temperature used to calculate H. If stack temperatures vary by more than 28°C (50°F), use the appropriate H value calculated in section 8.5.3 of this method. Calculate the dwell time at each traverse point as in equations 22 and 23. In addition to these procedures, you must also use running starts and stops on both small and large stacks if the static pressure at the sampling location is more negative than 5 in. water column. This prevents back pressure from rupturing the sample filter. If you use a running start, adjust the flow rate to the calculated value after you perform the leak check (see paragraph 8.4 of this method).

8.7.3.1 *Level and zero manometers*. Make periodic checks of the level and zero point of the manometers during the traverse. Vibrations and temperature changes may cause them to drift.

8.7.3.2 *Portholes*. Clean the portholes prior to the test run. This will minimize the chance of collecting deposited material in the nozzle.

8.7.3.3 *Sampling procedures*. Verify that the combined cyclone sampling head temperature is at stack temperature (± 10°C). Remove the protective cover from the nozzle. To begin sampling, immediat ely start the pump and adjust the flow to calculated isokinetic conditions. Position the probe at the first sampling point with the nozzle pointing directly into the gas stream. Ensure the probe/pitot tube assembly is leveled. [**Note:** When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.]

(a) You must traverse the stack cross-section, as required by Method 5. Do not bump the cyclone nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes. This will minimize the chance of extracting deposited materia ls.

(b) You must record the data required on the field test data sheet for each run. Record the initial dry gas meter reading. Then take dry gas meter readings at the following times: (1) the beginning and end of each sample time increment, (2) when changes in flow rates are made, and (3) when sampling is halted. Compare the velocity pressure measurements (Equations 20 and 21) with the velocity pressure measured during the preliminary traverse. Keep the meter box H at the value calculated in section 8.7.3 of this method for the stack temperature that is observed during the test. Record all

the point-by-point data and other source test parameters on the field test data sheet. Do not leak check the sampling system during port changes.

(c) Maintain the flow through the sampling system at the last sampling point. Remove the sampling train from the stack while you are still operating (running stop). Then stop the pump and record the final dry gas meter reading and other test parameters on the field test data sheet.

8.7.4 Process data. You must fully document the process and air pollution control system operating conditions during the test. This is important. You will need data and information on the process unit tested, the particulate control system used to control emissions, and the sampling train conditions.

8.7.4.1 *Particulate control system data*. You will use the process and particulate control system data to determine if representative operating conditions were maintained throughout the testing period.

8.7.4.2 *Sampling train data*. You will use the sampling train data to confirm that the measured particulate emissions are accurate and complete.

8.7.5 Sample recovery. First remove the sample head (combined cyclone/filter assembly) from the stack. After the sample head is removed, you must perform a post-test leak check of the probe and sample train. Then recover the components

from the cyclone/filter. Refer to the following sections for more detailed information.

8.7.5.1 *Remove sampling head*. At the conclusion of the test, document final test conditions and remove the pitot tube and combined cyclone sampling head from the source. Make sure that you do not scrape the pitot tube or the combined cyclone sampling head against the port or stack walls. [**Note:** After you stop the gas flow, make sure you keep the combined cyclone head level to avoid tipping dust from the cyclone cups into the filter and/or down-comer lines.] After cooling and when the probe can be safely handled, wipe off all external surfaces near the cyclone nozzle and cap the inlet to cyclone I. Remove the combined cyclone/filter sampling head from the probe. Cap the outlet of the filter housing to prevent particulate matter from entering the assembly.

8.7.5.2 *Leak check probe/sample train assembly (post-test)*. Leak check the remainder of the probe and sample train assembly (including meter box) after removing the combined cyclone head/filter. You must conduct the leak rate at a vacuum equal to or greater than the maximum vacuum achieved during the test run. Enter the results of the leak check onto the field test data sheet. If the leak rate of the sampling train (without the combined cyclone sampling head) exceeds 0.02 ACFM or 4% of the average sampling rate during the test run (whichever is less), the run is invalid and you must repeat it.

8.7.5.3 *Post-test Nitrogen Purge*. As soon as possible after the post-test leak check, detach the probe, cyclones, and filter from the impinger train. Leave the ice in the second impinger box to prevent removal of moisture during the purge. If necessary, add more ice during the purge to maintain the gas temperature below 20°C.

8.7.5.4 You must weigh or measure the volume of the liquid collected in the drop out, impingers, and silica trap. You must measure the liquid in the first impingers to within 1 mL using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present to be used to calculate the moisture content of the effluent gas.

8.7.5.5 If a balance is available in the field, you must weight the silica impinger to within 0.5 g. Note the color of the indicating silica gel in the last impinger to determine whether it has been complete ly spent, and make a notation of its condition. If a balance is not available in the field, leave the silica in the impinger for recovery after the post-test nitrogen purge is complete.

8.7.5.6 If no water was collected before the ambient filter, you may skip the remaining purge steps and proceed with sample recovery (see section 8.7.5.8 of this method and following).

8.7.5.7 The impinger tip must be below the water level in the combined catch impinger. If insufficient water was collected, you must add degassed

ASTM Type II or equivalent water until the impinger tip is at least 1 cm below the surface of the water.

8.7.5.8 With no flow of gas through the clean purge line and fittings, attach it to the input of the impinger train (see Figure 9 in Section 17). To avoid over- or under-pressurizing the impinger array, slowly commence the nitrogen gas flow through the line while simultaneously opening the meter box pump valve(s). Adjust the pump bypass and nitrogen delivery rates to obtain the following conditions: (1) 20 liters/min or $H_@$ and (2) an overflow rate through the rotameter of less than 2 liters/min. Condition (2) guarantees that the nitrogen delivery system is operating at greater than ambient pressure and prevents that possibility of passing ambient air (rather than nitrogen) through the impingers. Continue the purge under these conditions for 1 hour, checking the rotameter and H value(s) periodically. After 1 hour, simultaneously turn off the delivery and pumping systems.

8.7.5.9 *Recovery of particulate matter*. Recovery involves the quantitative transfer of particles in the following size range: (1) greater than 10 micrometers, (2) less than or equal to 10 micrometers but greater than 2.5 micrometers, and (3) less than or equal to 2.5 micrometers. You must use a Nylon brush and an ultrapure acetone rinse to recover particles from the combined cyclone/filter sampling head. Use the following procedures for each container.

Container #1 - Use tweezers and/or clean disposable surgical gloves to remove the filter from the filter holder. Place the filter in the petri dish you identified as Container #1. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer any particulate matter and/or filter fibers that adhere to the filter holder gasket or filter support screen to the petri dish. Seal the container. This container holds particles less than 2.5 micrometers that are caught on the in-stack filter.

Container #2 - Quantitatively recover the (1) particulate matter from the cyclone I cup and acetone rinses (and brush cleaning) of the cyclone cup, (2) internal surface of the nozzle, and (3) cyclone I internal surfaces, including the outside surface of the downcomer line. Seal the container and mark the liquid level on the outside of the container. You must keep any dust found on the outside of cyclone I and cyclone nozzle external surfaces out of the sample. This container holds particulate matter greater than 10 micrometers.

Container #3 - Place the solids from cyclone cup IV and the acetone (and brush cleaning) rinses of the cyclone I turnaround cup (above inner downcomer line), inside of the downcomer line, and interior surfaces of cyclone IV into your #3 container. Seal the container and mark the liquid level on the outside. This container holds particulate matter less than 10 micrometers but greater than 2.5 micrometers.

Container #4 - Retrieve the acetone rinses (and brush cleaning) of the exit tube of cyclone IV and the front half of the filter holder in container #4. Seal the container and mark the liquid level on the outside of the container. This container holds particulate matter that is less than 2.5 micrometers.

Container # 5 - Quantitativel y transfer liquid from the drop out and the impinger prior to the ambient filter into a clean sample bottle (glass or plastic). Rinse each impinger and the connecting glassware, including probe extension, condenser, and front half of the cold filter housing twice with water, recover the rinse water, and add it to the same sample bottle. Mark the liquid level on the bottle. This container holds the water soluble condensable particulate matter captured impingers.

Container # 6 - Follow the water rinses of each impinger and the connecting glassware, including the condenser, with an acetone, then repeat the entire procedure with two rinses of methylene chloride and save both solvents in a separate No. 2M container. Mark the liquid level on the jar.

Container # 7 - Use tweezers and/or clean disposable surgical gloves to remove the filter from the cold filter holder. Place the filter in the petri dish you identified as Container #7.

Container # 8 - If the water from the cold impinger has been weighed in the field it can be discarded, otherwise quantitatively transfer liquid from the cold impinger that follows the ambient filter into a clean sample bottle (glass or plastic). Mark the liquid level on the bottle. This container holds the remainder of the liquid water from the emission gases. The contents of Container #8 is weighed during sample analysis..

Container #9 Silica Gel Absorbent - Transfer the silica gel to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If the silica gel has been weighed in the field to measure water content it can be discarded, otherwise the contents of Container #9 is weighed during sample analysis.

Container #10 - Take 100 mL of the acetone directly from the wash bottle you used, and place it in Container #10, labeled Acetone Rinse Blank.

Container #11 - Take 100 mL of the water directly from the wash bottle you used, and place it in Container #9, labeled Water Rinse Blank.

Container #12 - Take 100 mL of the methylene chloride directly from the wash bottle you used, and place it in Container #12, labeled MeCl Rinse Blank.

8.7.6 Transport procedures. Containers must remain in an upright position at all times during shipping. You do not have to ship the containers under dry or blue ice.

## 9. QUALITY CONTROL

9.1 Daily Quality Checks

You must perform daily quality checks using data quality indicators that require review of (1) recording and transfer of raw data, (2) calculations, and (3) documentation of testing procedures.

9.2 Calculation Verification

You will verify the calculations by independent, manual checks. You must flag any suspect data and identify the nature of the problem and potential effect on data quality. After you complete the test, prepare a data summary and compile all the calculations and raw data sheets.

9.3 Conditions

You must record any unusual process operating conditions or adverse weather conditions that occur during testing. Discontinue the test if the operating conditions may cause non-representative particulate emissions.

9.4 Health and Safety Plan

You must also develop a health and safety plan to ensure the safety of your employees who are on-site conducting the particulate emission test. Your plan must conform with all applicable

OSHA, MSHA, and DOT regulatory requirements. The procedures must also conform to the plant health and safety requirements.

9.5 Calibration Checks

You must perform calibration check procedures on analytical balances each time they are used.

9.6 Glassware

You must use class A volumetric glassware for titrations or calibrate your equipment against NIST traceable glassware.

9.7 Audit Procedure

Concurrent with compliance sample analysis, you should analyze audit material to evaluate the technique of the analyst and the standards preparation. You will use the same staff, analytical reagents, and analytical system for both compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

9.8 Audit Samples

Audit samples will be supplied only to enforcement agencies for compliance tests. Audit sample can be requested by a state agency. Audit materials are requested online by authorized regulatory authorities at http://www .sscap.net/. Authorization can be obtained by contacting an EPA EMC QA Team Member listed on the EPA TTN Website

http://www.epa.gov/ttn/emc/email.html#qaqc . The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

9.9 Audit Results

Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency.

## 10. CALIBRATION AND STANDARDIZATION

[**Note**: Maintain a laboratory log of all calibrations.]

10.1 Gas flow velocities

Measure the gas flow velocities at the sampling locations using Method 2 of Appendix A to 40 CFR part 60. You must use an S-type pitot tube that meets the required EPA specifications (EPA Publication 600/4-77-0217b) during these velocity measurements. You must also complete the following:

(a) Visually inspect the S-type pitot tube before sampling.

(b) Leak check both legs of the pitot tube before and after sampling.

(c) Maintain proper orientation of the S-type pitot tube while making measurements.

10.1.1 S-type pitot tube orientation. The S-type pitot tube is oriented properly when the yaw and the pitch axis are 90 degrees to the air flow.

10.1.2 Average velocity pressure record. Instead of recording either high or low values, record the average velocity pressure at each point during flow measurements.

10.1.3 Pitot tube coefficient. Determine the pitot tube coefficient based on physical measurement techniques described in Method 2 of Appendix A to 40 CFR part 60. [**Note:** You must calibrate the pitot tube on the sampling head because of potential interferences from the cyclone body. Refer to paragraph 8.7.2 under the Sample Collection, Preservation, Storage and Transport section of this method for additional information.]

10.2 Thermocouple calibration

You must calibrate the thermocouples using the procedures described in paragraph 10.1.4.1.2 of Method 2 of Appendix A to 40 CFR part 60 to calibrate the thermocouples. Calibrate each temperature sensor at a minimum of three points over the anticipated range of use against an NIST-traceable mercury-in-glass thermometer.

10.3 Nozzles

You may use stainless steel (316 or equivalent) or Teflon®-coated nozzles for isokinetic sampling. Make sure that all nozzles are thoroughly cleaned, visually inspected, and calibrated according to the procedure outlined in paragraph 10.1 of Method 5 of Appendix A to 40 CFR part 60.

10.4 Dry gas meter calibration

You must calibrate your dry gas meter following the calibration procedures in paragraph 16.1 of Method 5 of Appendix A to 40 CFR part 60. Also, make sure you fully calibrate the dry gas meter to determine the volume correction factor prior to field use. Post-test calibration checks must be performed as soon as possible after the equipment has been returned to the shop. Your pretest and post-test calibrations must agree within ±5 percent.

## 11. ANALYTICAL PROCEDURES

11.1 Analytical data sheet

Record all data on the analytical data sheet. Obtain the data sheet from Figure 5-6 of Method 5 of Appendix A to 40 CFR part 60.

11.2 Dry weight of particulate matter

Determine the dry weight of particulate following procedures outlined in this section. Record the data required on a sheet such as the one shown in Figure 10 in the Tables, Diagrams, Flowcharts, and Validation Data section of this method.

11.2.1 Container #1-PM2.5 Micron filterable particulate. Transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate or indicating silica gel. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

11.2.2 Container #2-PM10 and greater filterable particulate. Separately treat this container like Container #1.

11.2.3 Container #3-Filterable particulate less than 10 microns and greater than 2.5 micron. Separately treat this container like Container #1.

11.2.4 Container #4-Acetone rinses of the exit tube of cyclone IV and front half of the filter holder. Note the level of liquid in the container, and confirm on the analysis

sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.5 Methylene Chloride Impinger Rinse (Container 6). See instruction in section 11.2.6.1 of this method.

11.2.6 Container 6, Aqueous Liquid Impinger Contents. You must analyze the condensable particulate sample in containers 5 and 6 as described in this section. See the flow chart in Figure 11 of the Tables, Diagrams, Flowcharts, and Validation Data section of this test method. First, note the level of liquid in each container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g.

11.2.6.1 *Organic Extraction*. Separate the organic fraction of the sample by adding the contents of Container No. 5 (acetone and methylene chloride) to the contents of Container No. 6 in a 1000-ml separatory funnel. After mixing, allow the aqueous and organic phases to fully separate. If there is no clear separation between the organic phase and

the water, add deionized water meeting the method specifications until a separation occurs. Drain off most of the organic/methylene chloride phase and save in a clean container. Then add 30 mL of methylene chloride to the funnel, mix well, and drain off the lower organic phase. Repeat with another 30 mL of methylene chloride. This extraction should yield about 100 mL of organic extract. Each time, leave a small amount of the organic/methylene chloride phase in the separatory funnel ensuring that no water is collected in the organic phase.

11.2.6.2 *Organic Fraction Weight Determination (Organic Phase from Container Nos. 5 and 6).* Place the organic extract in a tared 250-mL clean glass beaker. Evaporate the organic extract at room temperature and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50 mL preweighed tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg.

11.2.6.3 *Inorganic Fraction Weight Determination* . Transfer the aqueous fraction from the extraction to a tared 250 mL beaker and evaporate to near dryness (less than 10 mL liquid) in the oven and then allow to air dry at ambient temperature. Redissolve the residue in 100 ml of ASTM Type II water or equivalent. Remove a 1 mL aliquote.

11.2.6.4 Use titration to neutralize acid in the sample and remove water of hydration. Titrate the sample with 0.1N ammonia hydroxide to a pH of 7.0, as indicated by a pH meter. Record the volume of titrant used.

11.2.6.5 Using an oven at 105°C, evaporate the aqueous phase to approximately 10 ml; then, evaporate to dryness at room temperature and pressure. Desiccate the dry sample for 24 hours, weigh to a constant weight, and record the results to the nearest 0.1 mg.

Note: The 0.1 N $NH_4OH$ is made as follows: Add 7 ml of concentrated (14.8 M) $NH_4OH$ to 1 liter of water. Standardize against standardized 0.1 N $H_2SO_4$ and calculate the exact normality using a procedure parallel to that described in section 5.5 of Method 6 (Appendix A, 40 CFR Part 60). Alternatively, purchase 0.1 N $NH_4OH$ that has been standardized against a National Institute of Standards and Technology reference material.

11.2.6.6 Calculate the correction factor to subtract the $NH_4^+$ retained in the sample using equation 46.

11.2.7 Container #7 (Cold Filter Sample). You must dry the filter recovered from the ambient temperature portion of the train until it reaches constant weight. The filter may be dried at room temperature in a laboratory hood until condensed water has evaporated. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate or indicating silica gel. Weigh to a constant weight and report the results to the nearest 0.1 mg.

11.2.8 Container #8 (Cold impinger water). If the amount of water has not been determined in the field, note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g.

11.2.9 Container #9 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.10 Analysis of Acetone Blank (Container No. 10). Use 100 mL of methylene chloride from the blank container for this analysis. Measure the acetone in this container either volumetrically or gravimetrically . Transfer 100 mL of the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight . Report the results to the nearest 0.1 mg.

11.2.11 Analysis of Water (Container #11). Analyze the water used for sample recovery as follows: First, note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. Remove 100 mL for analysis. If insufficient liquid is available or if the water has been lost due to container breakage either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. You must perform organic residual analysis as described in sections 11.6.2.1 and 11.6.2.2 of this

method. You must also perform residual inorganic analysis as described in section 11.2.6.3 of this method.

11.2.12 Analysis of Methylene Chloride Blank (Container Nos. 12). You must use 100 mL of methylene chloride from the blank container for this analysis. Analyze these sample blanks as described in section 11.2.6.2 of this method.

## 12. CALCULATIONS AND DATA ANALYSIS

12.1 What do I need to calculate?

You need to perform all of the calculations found in Table 3 of this paragraph. Table 3 of this paragraph also provides instructions and references for the calculations.

Table 3. Calculations for Recovery of $PM_{10}$ and $PM_{2.5}$

| Calculations | Instructions and References |
|---|---|
| Average dry gas meter temperature | See field test data sheet. |
| Average orifice pressure drop | See field test data sheet. |
| Dry gas volume ($V_{ms}$) | Use Equation 27 to correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in. Hg). |
| Dry gas sampling rate ($Q_{sST}$) | Must be calculated using Equation 28. |
| Volume of water condensed ($V_{ws}$) | Use Equation 29 to determine the water condensed in the impingers and silica gel combination. Determine the total moisture catch by measuring the change in volume or weight in the impingers and weighing the silica gel. |
| Moisture content of stack gas ($B_{ws}$) | Calculate this with Equation 30. |

Table 3. Calculations for Recovery of $PM_{10}$ and $PM_{2.5}$

| Calculations | Instructions and References |
|---|---|
| Gas sampling rate ($Q_s$) | Calculate this with Equation 31. |
| Test condition Reynolds number[1] | Use Equation 8 to calculate the actual Reynolds number during test conditions. |
| Actual $D_{50}$ of Cyclone I | Calculate this with Equation 32. This calculation is based on the average temperatures and pressures measured during the test run. |
| Stack gas velocity ($v_s$) | Calculate this with Equation 11. |
| Percent isokinetic rate (%I) | Calculate this with Equation 40. |

[1] Calculate the Reynolds number at the cyclone IV inlet during the test based on: (1) the sampling rate for the combined cyclone head, (2) the actual gas viscosity for the test, and (3) the dry and wet gas stream molecular weights.

12.2 What data must I analyze?

You must analyze $D_{50}$ of cyclone IV and the concentrations of the particulate matter in the various size ranges.

12.2.1 $D_{50}$ of cyclone IV. To determine the actual $D_{50}$ for cyclone IV, recalculate the Cunningham correction factor and the Reynolds number for the best estimate of cyclone IV $D_{50}$. The following paragraphs describe additional information on how to recalculate the Cunningham correction factor and determine which Reynold's number to use.

12.2.1.1 *Cunningham correction factor*. Recalculate the initial estimate of the Cunningham correction factor using the actual test data. Insert the actual test run data and $D_{50}$ of 2.5 micrometers into Equation 4. This will give you a new Cunningham correction factor that is based on actual data.

12.2.1.2 *Initial $D_{50}$ for cyclone IV*. Determine the initial estimate for cyclone IV $D_{50}$ using the test condition Reynolds number calculated with Equation 8 as indicated in Table 3 of this section. Refer to the following instructions.

(a) If the Reynold's number is less than 3162, calculate the $D_{50}$ for cyclone IV with Equation 33, using actual test data.

(b) If the Reynold's number is equal to or greater than 3162, calculate the $D_{50}$ for cyclone IV with Equation 34, using actual test data.

(c) Insert the "new" $D_{50}$ value calculated by either Equation 33 or 34 into Equation 35 to re-establish the Cunningham Correction Factor ($C_r$). [**Note:** Use the test condition calculated Reynolds number to determine the most appropriate equation (Equation 33 or 34).]

12.2.1.3 *Re-establish cyclone IV $D_{50}$*. Use the re-established Cunningham correction factor (calculated in the previous step) and the calculated Reynold's number to determine $D_{50\text{-}1}$.

(a) Use Equation 36 to calculate the re-established cyclone IV $D_{50-1}$ if the Reynolds number is less than 3162.

(b) Use Equation 37 to calculate the re-established cyclone IV $D_{50-1}$ if the Reynolds number is equal to or greater than 3162.

12.2.1.3 *Establishing "Z" values*. The "Z" value is the result of an analysis that you must perform to determine if the Cunningham correction factor is acceptable. Compare the calculated cyclone IV $D_{50}$ (either Equation 33 or 34) to the re-established cyclone IV $D_{50-1}$ (either Equation 36 or 37) values based upon the test condition calculated Reynolds number (Equation 38, refer to 2.1.2 for additional information). Follow these procedures.

(a) Use Equation 38 to calculate the "Z". If the "Z" value is within 0.99 and 1.01, then the $D_{50-1}$ value is the best estimate of the cyclone IV $D_{50}$ cut diameter for your test run.

(b) If the "Z" value is greater than 1.01 or less than 0.99, re-establish a Cunningham correction factor based on the $D_{50-1}$ value determined in either Equations 36 or 37, depending upon the test condition Reynolds number.

(c) Use the second revised Cunningham correction to re-calculate the cyclone IV $D_{50}$.

(d) Repeat this iterative process as many times as necessary using the prescribed equations until you achieve the criteria documented in Equation 39.

12.2.2 Particulate concentration. Use the particulate catch weights in the combined cyclone sampling train to calculate the concentration of particulate matter in the various size ranges. You must correct the concentrations for the acetone blank.

12.2.2.1 *Acetone blank concentration*. Use Equation 41 to calculate the acetone blank concentration ($C_a$).

12.2.2.2 *Acetone blank weight*. Use Equation 42 to calculate the acetone blank weight ($W_a$). [**Note:** Correct each of the particulate matter weights per size fraction by subtracting the acetone blank weight (that is, $M_{2,3,4}$-$W_a$)].

12.2.2.3 *Particulate weight catch per size fraction*. Subtract the weight of the acetone blank from the particulate weight catch in each size fraction. [**Note:** Do not subtract a blank value of greater than 0.001 percent of the weight of the acetone used from the sample weight.] Use the following procedures.

(a) Use Equation 43 to calculate the particulate matter recovered from Containers #1, #2, #3, and #4. This is the total collectable particulate matter ($C_{total}$).

(b) Use Equation 44 to determine the quantitative recovery of $PM_{10}$ particulate matter ($C_{PM10}$) from Containers #1, #3, and #4.

(c) Use Equation 45 to determine the quantitative recovery of $PM_{2.5}$ particulate ($C_{PM2.5)}$ recovered from Containers #1 and #4.

12.3 What must I include in the emission test report?

You must include the following list of conventional elements in the emissions test report.

(a) Emission test description including any deviations from this protocol

(b) Summary data tables on a run-by-run basis

(c) Flowchart of the process or processes tested

(d) Sketch of the sampling location

(e) Preliminary traverse data sheets including cyclonic flow checks

(f) Raw field data sheets

(g) Laboratory analytical sheets and case narratives

(h) Sample calculations

(i) Pretest and post-test calibration data

(j) Chain of custody forms

(k) Documentation of process and air pollution control system data

12.4 What nomenclature do I use in this method?

Use the following equations to complete the calculations required in this test method.

Molecular Weight of Dry Gas. This equation is similar to the equation in Method 201A of Appendix M to 40 CFR part 51.

$$M_d = 0.44(\%CO_2) + 0.32(\%O_2) + 0.28(100 - \%O_2 - \%CO_2) \quad \text{Equation 1}$$

Molecular Weight of Wet Gas. This equation is identical to the equation shown in Method 201A of Appendix M to 40 CFR part 51.

$$M_w = M_d(1 - B_{ws}) + 18(B_{ws}) \qquad \text{Equation 2}$$

Gas Viscosity. This equation is identical to the equation shown in previous versions of Method 201A of Appendix M to 40 CFR part 51 with the exception that the constants shown above are used for gas temperatures in °R, while the equation shown in Method 201A of Appendix M to 40 CFR part 51 had constants intended for gas temperatures in °F. The latest released version of Method 201A of Appendix M to 40 CFR part 51 has a viscosity equation that predicts values within 0.5% of Equation 1.

$$\mu = C_1 + C_2\sqrt{T_s} + C_3 T_s^{-2} + C_4(\%O_{2,wet}) - C_5 B_{ws} + C_6 B_{ws} T_s^2 \qquad \text{Equation 3}$$

Cunningham Correction Factor. The Cunningham correction factor is calculated for a 2.25 micrometer diameter particle.

$$C = 1 + 0.0057193\left[\frac{\mu}{P_s D_p}\right]\left[\frac{T_s}{M_w}\right]^{0.5} \qquad \text{Equation 4}$$

Lower Limit Cut Diameter for Cyclone I for $N_{re} < 3162$. The Cunningham correction factor is for a 2.25 micrometer diameter particle.

$$D_{50LL} = 9.507C^{0.3007}\left[\frac{M_w P_s}{T_s}\right]^{0.1993} \qquad \text{Equation 5 } (N_{re} < 3162)$$

Cut Diameter for Cyclone I for the Middle of the Overlap Zone.

$$D_{50T} = \left( \frac{11 + D_{50LL}}{2} \right)$$ Equation 6

Sampling Rate.

$$Q_s = Q_1 = 0.07296(\mu)\left[\frac{T_s}{M_w P_s}\right]^{0.2949}\left[\frac{1}{D_{50T}}\right]^{1.4102}$$ Equation 7

Reynolds Number.

$$N_{re} = 8.64\times10^5\left[\frac{P_s M_w}{T_s}\right]\left[\frac{Q_s}{\mu}\right]$$ Equation 8

Meter Box Orifice Pressure Drop. This equation is identical to the equation presented in Method 201A of Appendix M to 40 CFR part 51.

$$\Delta H = \left[\frac{Q_s(1 - B_{ws})P_s}{T_s}\right]^2\left[\frac{1.083 T_m M_d \Delta H_@}{P_{bar}}\right]$$ Equation 9

Lower Limit Cut Diameter for Cyclone I for $N_{re} \geq 3162$. The Cunningham correction factor is for a 2.25 micrometer diameter particle.

$$D_{50LL} = 10.0959 C^{0.4400}\left[\frac{M_w P_s}{T_s}\right]^{0.0600}$$ Equation 10 ($N_{re} \geq 3162$)

Velocity of Stack Gas. Correct the mean preliminary velocity pressure for Cp and blockage using Equations 23, 24, and 25.

$$v_s = K_p C_p \sqrt{(\Delta p)_{avg}} \left[ \sqrt{\frac{T_s}{P_s M_w}} \right] \qquad \text{Equation 11}$$

Calculated Nozzle Diameter for Acceptable Sampling Rate.

$$D = \left[ \frac{3.056\ Q_s}{v_s} \right]^{0.5} \qquad \text{Equation 12}$$

Velocity of Gas in Nozzle.

$$V_n = \frac{\left( \frac{Q_s}{60} \right)}{A_n} \qquad \text{Equation 13}$$

Minimum Nozzle/Stack Velocity Ratio Parameter.

$$R_{min} = \left[ 0.2457 + \left( 0.3072 - \frac{0.2603(\mu)(Q_s)^{0.5}}{v_n^{1.5}} \right)^{0.5} \right] \qquad \text{Equation 14}$$

Maximum Nozzle/Stack Velocity Ratio Parameter. Equations 14 and 15 are identical to equations presented in Method 201A of Appendix M to 40 CFR part 51.

$$R_{max} = \left[0.4457 + \left(0.5690 + \frac{0.2603(\mu)(Q_s)^{0.5}}{v_n^{1.5}}\right)^{0.5}\right] \quad \text{Equation 15}$$

Minimum Gas Velocity for $R_{min} \leq 0.5$.

$$v_{min} = v_n(0.5) \quad \text{Equation 16}$$

Minimum Gas Velocity for $R_{min} > 0.5$.

$$v_{min} = v_n R_{min} \quad \text{Equation 17}$$

Equations 16 and 17 are identical to equations presented in Method 201A of Appendix M to 40 CFR part 51.

Maximum Gas Velocity for $R_{max} \leq 1.5$.

$$v_{max} = v_n R_{max} \quad \text{Equation 18}$$

Maximum Gas Velocity for $R_{max} > 1.5$.

$$v_{max} = v_n(1.5) \quad \text{Equation 19}$$

Minimum Velocity Pressure.

$$\Delta p_{min} = 1.3686 \times 10^{-4}\left[\frac{P_s M_w}{T_s}\right]\left[\frac{v_{min}}{C_p}\right]^2 \quad \text{Equation 20}$$

Maximum Velocity Pressure.

$$\Delta p_{max} = 1.3686 \times 10^{-4} \left[\frac{P_s M_w}{T_s}\right]\left[\frac{v_{max}}{C_p}\right]^2 \qquad \text{Equation 21}$$

Sampling Time at Point 1. $N_p$ is the total number of traverse points. Equation 22 is identical to an equation presented in Method 201A of Appendix M to 40 CFR part 51. You must use the preliminary velocity traverse data.

$$t_1 = \left[\frac{\sqrt{\Delta p_1}}{\sqrt{\Delta p_{avg}}}\right]\left[\frac{t_t}{N_p}\right] \qquad \text{Equation 22}$$

Sampling Time at Point n. You must use the actual test run data at each point, n, and test run point 1.

$$t_n = t_1 \frac{\sqrt{\Delta p_n}}{\sqrt{\Delta p_1}} \qquad \text{Equation 23}$$

Adjusted Velocity Pressure.

$$\Delta p_s = \Delta p_m \left[\frac{C_p}{C_p'}\right]^2 \qquad \text{Equation 24}$$

Average Probe Blockage Factor.

$$b_f = \frac{12.0}{A}$$ Equation 25

Velocity Pressure.

$$\Delta p_{s2} = \Delta p_{s1}\left[\frac{1}{(1 - b_f)}\right]^2$$ Equation 26

Dry Gas Volume Sampled at Standard Conditions.

$$V_{ms} = \left[\frac{528}{29.92}\right]\left[\gamma V_m\right]\left[\frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m}\right]$$ Equation 27

Sample Flow Rate at Standard Conditions.

$$Q_{sst} = \frac{V_{ms}}{\theta}$$ Equation 28

Volume of Water Vapor.

$$V_{ws} = 0.04707 V_c$$ Equation 29

Moisture Content of Gas Stream.

$$B_{ws} = \left[\frac{V_{ws}}{V_{ms} + V_{ws}}\right]$$ Equation 30

Sampling Rate.

$$Q_s = \frac{29.92}{528} Q_{sdT} \left[\frac{1}{(1 - B_{ws})}\right]\left[\frac{T_s}{P_s}\right] \qquad \text{Equation 31}$$

Note: The viscosity and Reynolds Number must be recalculated using the actual stack temperature, moisture, and oxygen content.

Actual Particle Cut Diameter for Cyclone I. This is based on actual temperatures and pressures measured during the test run.

$$D_{50} = 0.15625 \left[\frac{T_s}{M_w P_s}\right]^{0.2091} \left[\frac{\mu}{Q_s}\right]^{0.7091} \qquad \text{Equation 32}$$

Particle Cut Diameter for $N_{re} < 3162$ for Cyclone IV. C must be recalculated using the actual test run data and a $D_{50}$ ($D_p$) of 2.5.

$$D_{50} = 0.0024302 \left[\frac{\mu}{Q_s}\right]^{1.1791} \left[\frac{1}{C}\right]^{0.5} \left[\frac{T_s}{P_s M_w}\right]^{0.6790} \qquad \text{Equation 33 } (N_{re} < 3162)$$

Particle Cut Diameter for $N_{re} \geq 3162$ for Cyclone IV. C must be recalculated using the actual test run data and a $D_{50}$ ($D_p$) of 2.5.

$$D_{50} = 0.019723\left[\frac{\mu}{Q_s}\right]^{0.8058}\left[\frac{1}{C}\right]^{0.5}\left[\frac{T_s}{P_s M_w}\right]^{0.3058}$$ Equation 34 ($N_{re} \geq 3162$)

Re-estimated Cunningham Correction Factor. You must use the actual test run Reynolds Number ($N_{re}$) value and select the appropriate $D_{50}$ from Equation 32 or 33 (or Equation 36 or 37 if reiterating).

$$C_r = 1 + 0.0057193\left[\frac{\mu}{P_s D_{50}}\right]\left[\frac{T_s}{M_w}\right]^{0.5}$$ Equation 35

Re-calculated Particle Cut Diameter for $N_{re} < 3162$.

$$D_{50-1} = 0.0024302\left[\frac{\mu}{Q_s}\right]^{1.1791}\left[\frac{1}{C_r}\right]^{0.5}\left[\frac{T_s}{P_s M_w}\right]^{0.6790}$$ Equation 36 ($N_{re} < 3162$)

Re-calculated Particle Cut Diameter for $N_{re} \geq 3162$.

$$D_{50-1} = 0.019723\left[\frac{\mu}{Q_s}\right]^{0.8058}\left[\frac{1}{C_r}\right]^{0.5}\left[\frac{T_s}{P_s M_w}\right]^{0.3058}$$ Equation 37 ($N_{re} \geq 3162$)

Ratio (Z) Between $D_{50}$ and $D_{50-1}$ Values.

$$Z = \frac{D_{50-1}}{D_{50}}$$ Equation 38

Acceptance Criteria for Z Values. The number of iterative steps is represented by N.

$$0.99 \le \left[ Z = \left( \frac{D_{50_N}}{D_{50_{N+1}}} \right) \right] \le 1.01 \qquad \text{Equation 39}$$

Percent Isokinetic Sampling.

$$I = \left( \frac{100 T_s V_{ms} 29.92}{60 v_s \theta A_n P_s (1 - B_{ws}) 528} \right) \qquad \text{Equation 40}$$

Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Equation 41}$$

Acetone Blank Weight.

$$W_a = c_a V_{awpa} \qquad \text{Equation 42}$$

Concentration of Total Filterable Collectable Particulate Matter.

$$C_{ft} = \left( \frac{7000}{453,592} \right) \left[ \frac{M_1 + M_2 + M_3 + M_4}{V_{ms}} \right] \qquad \text{Equation 43}$$

Concentration of $PM_{10}$ Collectable Particulate Matter.

$$C_{fPM10} = \left(\frac{7000}{453,592}\right)\left[\frac{M_1 + M_3 + M_4}{V_{ms}}\right] \quad \text{Equation 44}$$

Concentration of $PM_{2.5}$ Collectable Particulate Matter.

$$C_{fPM2.5} = \left(\frac{7000}{453,592}\right)\left[\frac{M_1 + M_4}{V_{ms}}\right] \quad \text{Equation 45}$$

Correction for Ammonia added during Titration.

$$C_{NH_4} = \frac{48.03\ V_t\ N}{100} \quad \text{Equation 46}$$

Where:

48.03 = mg/meq. ammonia minus two hydrogen.

100 = Volume of solution, ml.

Mass of Inorganic CPM.

$$m_i = m_r \frac{V_{ic}}{V_{ic} - V_b} - m_c \quad \text{Equation 47}$$

Concentration of CPM.

$$C_{cpm} = \frac{m_o + m_i - m_b}{V_{ms}} \quad \text{Equation 48}$$

Total Collectable Particulate matter.

$$C_t = C_{tf} + C_{CPM} \quad \text{Equation 49}$$

Total $PM_{10}$ Collectable Particulate matter.

$$C_{tPM10} = C_{fPM10} + C_{CPM} \quad \text{Equation 50}$$

Total $PM_{2.5}$ Collectable Particulate matter.

$$C_{tPM2.5} = C_{fPM2.5} + C_{CPM} \quad \text{Equation 51}$$

## 13. METHOD PERFORMANCE

[Reserved]

## 14. POLLUTION PREVENTION

[Reserved]

## 15. WASTE MANAGEMENT

[Reserved]

## 16. REFERENCES

We used the following references to develop this test method:

1. Dawes, S.S., and W.E. Farthing. "Application Guide for Measurement of $PM_{2.5}$ at Stationary Sources," U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, 27511, EPA-600/3-90/057 (NTIS No.: PB 90-247198), November 1990.

2. U.S. Environmental Protection Agency, Federal Reference Methods 1 through 5 and Method 17, 40 CFR 60, Appendix A.

3. U.S. Environmental Protection Agency, Federal Reference Method 201A, 40 CFR 51, Appendix M.

4. Richards, J.R. "Test protocol: PCA $PM_{10}/PM_{2.5}$ Emission Factor Chemical Characterization Testing," PCA R&D Serial No. 2081, Portland Cement Association, 1996.

5. DeWees, W.D., S.C. Steinsberger, G.M. Plummer, L.T. Lay, G.D. McAlister, and R.T. Shigehara. "Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensible Matter from Stationary Sources." Paper presented at the 1989 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants. Raleigh, North Carolina. May 1-5, 1989.

6. DeWees, W.D. and K.C. Steinsberger. "Method Development and Evaluation of Draft Protocol for Measurement of Condensible Particulate Emissions." Draft Report. November 17, 1989.

7. Texas Air Control Board, Laboratory Division. "Determination of Particulate in Stack Gases Containing Sulfuric Acid and/or Sulfur Dioxide." Laboratory Methods for Determination of Air Pollutants. Modified December 3, 1976.

8. Nothstein, Greg. Masters Thesis. University of Washington. Department of Environmental Health. Seattle, Washington.

9. "Particulate Source Test Procedures Adopted by Puget Sound Air Pollution Control Agency Board of Directors." Puget Sound Air Pollution Control Agency, Engineering Division. Seattle, Washington. August 11, 1983.

10. Commonwealth of Pennsylvania, Department of Environmental Resources. Chapter 139, Sampling and Testing (Title 25, Rules and Regulations, Part I, Department of Environmental Resources, Subpart C, Protection of Natural Resources, Article III, Air Resources). January 8, 1960.

11. Wisconsin Department of Natural Resources. Air Management Operations Handbook, Revision 3. January 11, 1988.

**17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA**

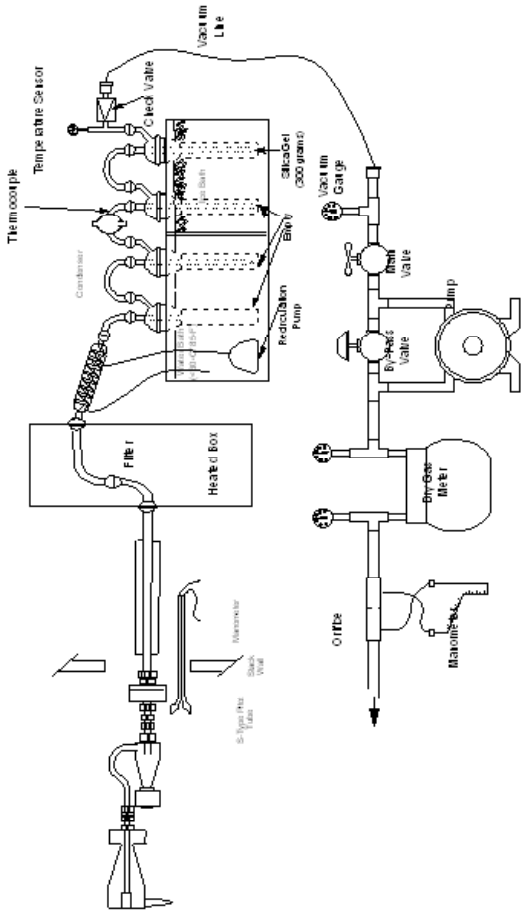



**Figure 1. PM2.5 Sampling Train**

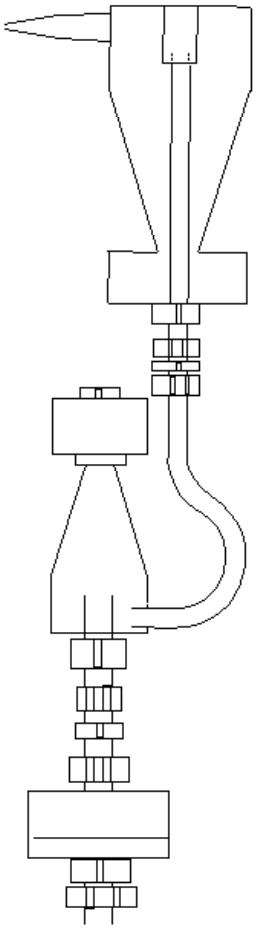
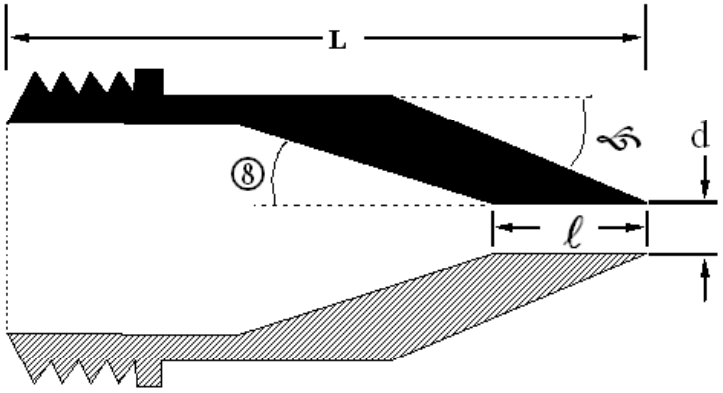
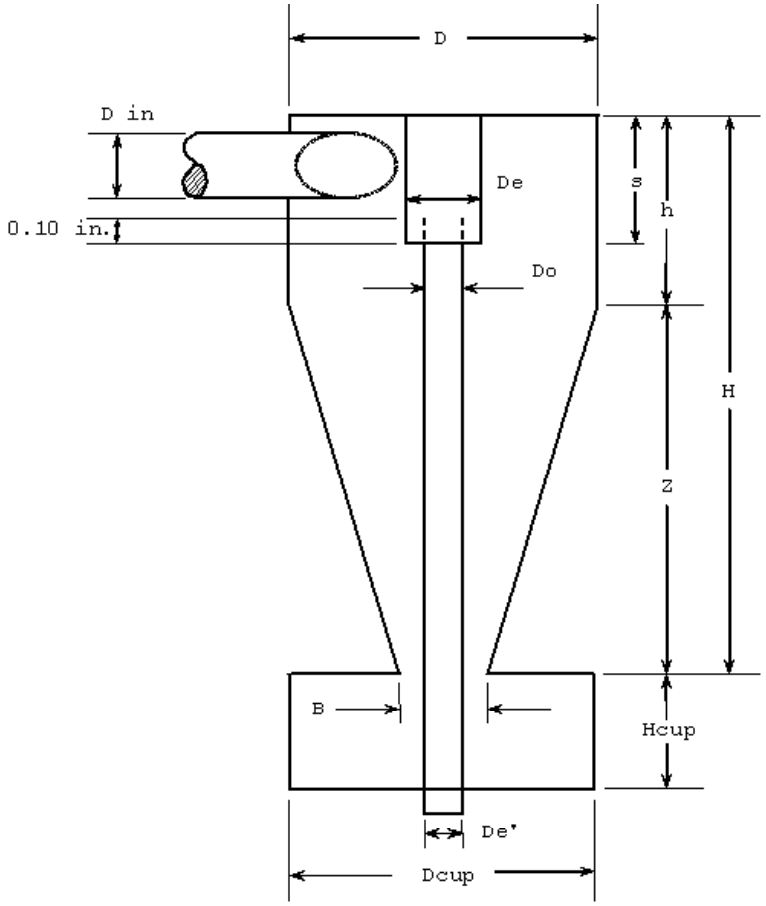


**Figure 2. Combined Cyclone Sampling Head**



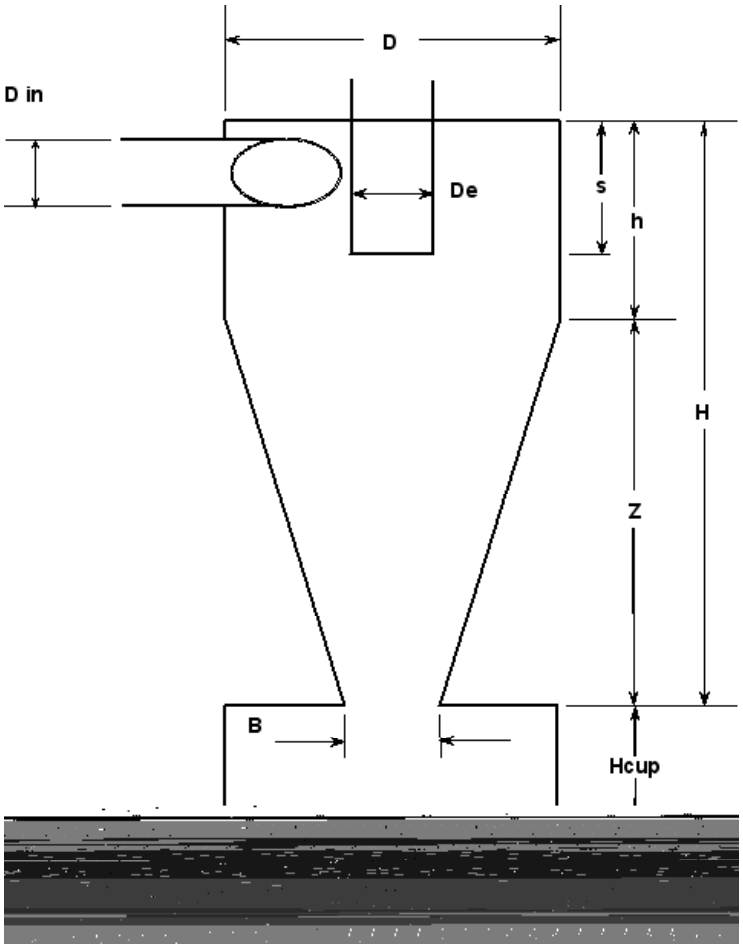

| Nozzle diameter, d (inches) | Cone Angle, q (degrees) | Outside taper, f (degrees) | Straight inlet length, l (inches) | Total Length, L (inches) |
|---|---|---|---|---|
| 0.125 | 4 | 15 | <0.05 | 2.710±0.05 |
| 0.136 | 4 | 15 | <0.05 | 2.653±0.05 |
| 0.150 | 4 | 15 | <0.05 | 2.553±0.05 |
| 0.164 | 5 | 15 | <0.05 | 1.970±0.05 |
| 0.180 | 6 | 15 | <0.05 | 1.572±0.05 |
| 0.197 | 6 | 15 | <0.05 | 1.491±0.05 |
| 0.215 | 6 | 15 | <0.05 | 1.450±0.05 |
| 0.233 | 6 | 15 | <0.05 | 1.450±0.05 |
| 0.264 | 5 | 15 | <0.05 | 1.450±0.05 |
| 0.300 | 4 | 15 | <0.05 | 1.480±0.05 |
| 0.342 | 4 | 15 | <0.05 | 1.450±0.05 |
| 0.390 | 3 | 15 | <0.05 | 1.450±0.05 |

**Figure 3. Nozzle Design Specifications**




| Cyclone I (10 Micrometer) | Cyclone Interior Dimensions (cm ± 0.02 cm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Din | D | De | B | H | h | Z | S | Hcup | Dcup | De' | Do |
| | 1.27 | 4.47 | 1.50 | 1.88 | 6.95 | 2.24 | 4.71 | 1.57 | 2.25 | 4.45 | 1.02 | 1.24 |

**Figure 4. Design Specifications for Cyclone I (10 Micrometer)**




| Cyclone | Cyclone Interior Dimensions (cm ± 0.02 cm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| IV | Din | D | De | B | H | h | Z | S | Hcup | Dcup |
| (2.5 Micrometer) | 0.51 | 2.54 | 0.59 | 1.09 | 2.68 | 1.03 | 1.65 | 0.58 | 2.22 | 2.62 |

**Figure 5. Design Specifications for Cyclone IV (2.5 Micrometer) Sizing Device**

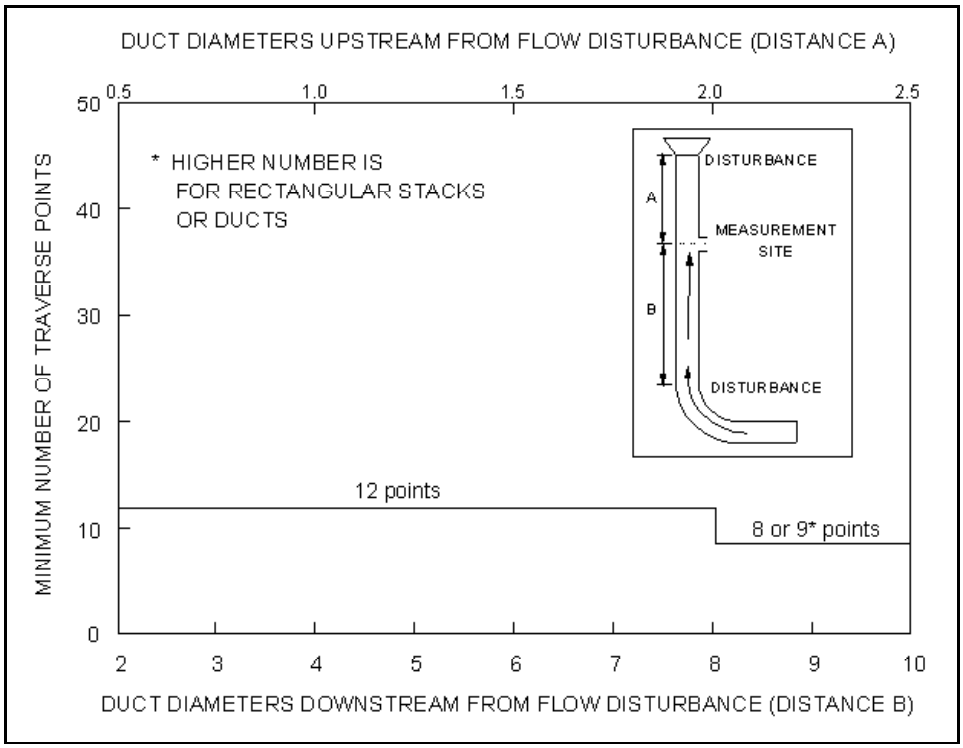



**Figure 6. Minimum Number of Traverse Points for Preliminary Method 4 Traverse**

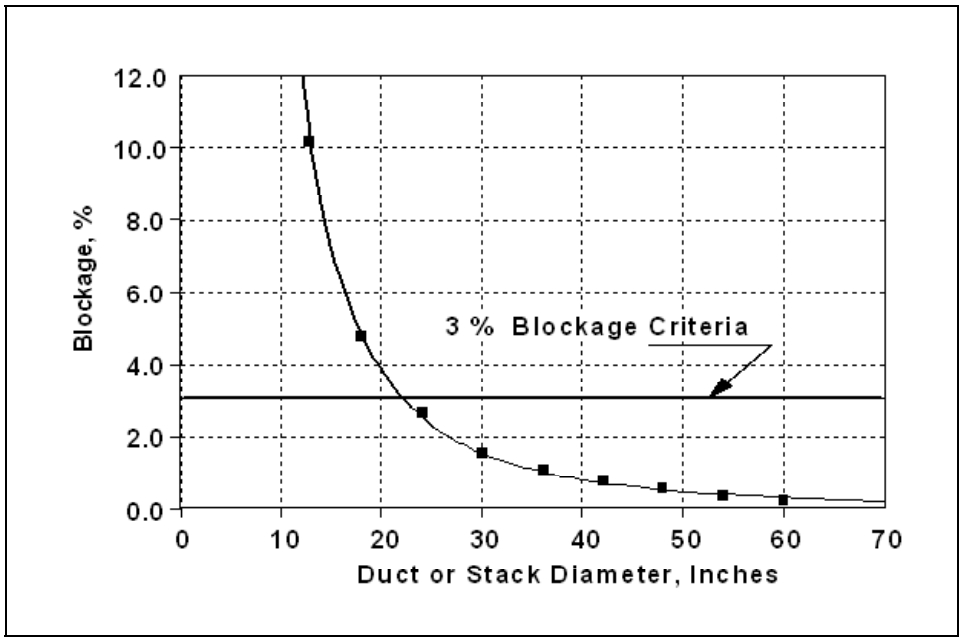



**Figure 7. Gas Flow Blockage by the Combined Cyclone Sampling Head**

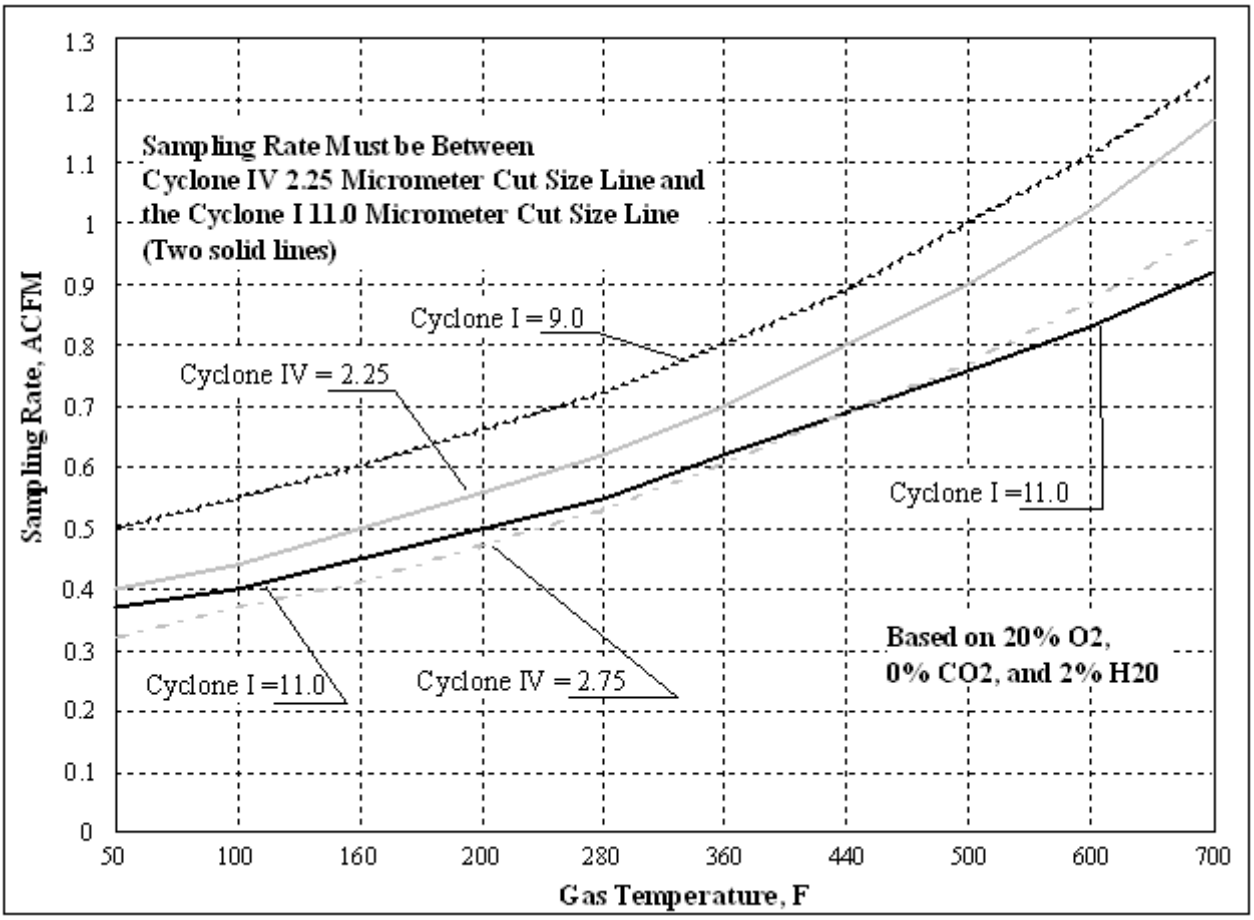



**Figure 8. Acceptable Sampling Rate for Combined Cyclone Heads**

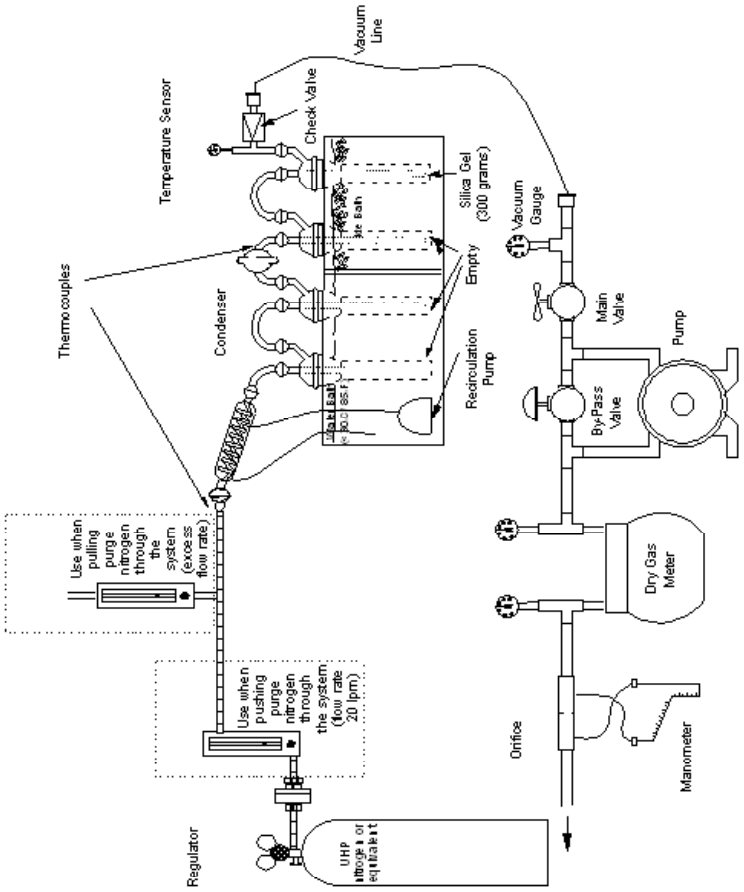



**Figure 9. Nitrogen Purge Train Configuration**

**Moisture Determination**

Volume or weight of liquid in impingers_____ _____ ml or g
Weight of moisture in silica gel_____ g

**Sample Preparation (Container No. 4)**

Amount of liquid lost during transport_ _____ ml
Final volume _____ ml
pH of sample prior to analysis_____
Addition of $NH_4OH$ required? _____
Sample extracted 2X with 75 ml methylene chloride? _____

**For Titration of Sulfate**

Normality of $NH_4OH$ _____ N
Volume of sample titrated _____ ml
Volume of titrant _____ ml

**Sample Analysis**

| | Weight of Condensible Particulate, mg | | |
|---|---|---|---|
| Container number | Final Weight | Tare Weight | Weight Gain |
| 4 (Inorganic) | | | |
| 4 & 5 (Organic) | | | |
| | | Total | |
| | | Less Blank | |
| | | Weight of Condensible Particulate | |

**Figure 10. Analytical Data Sheet**

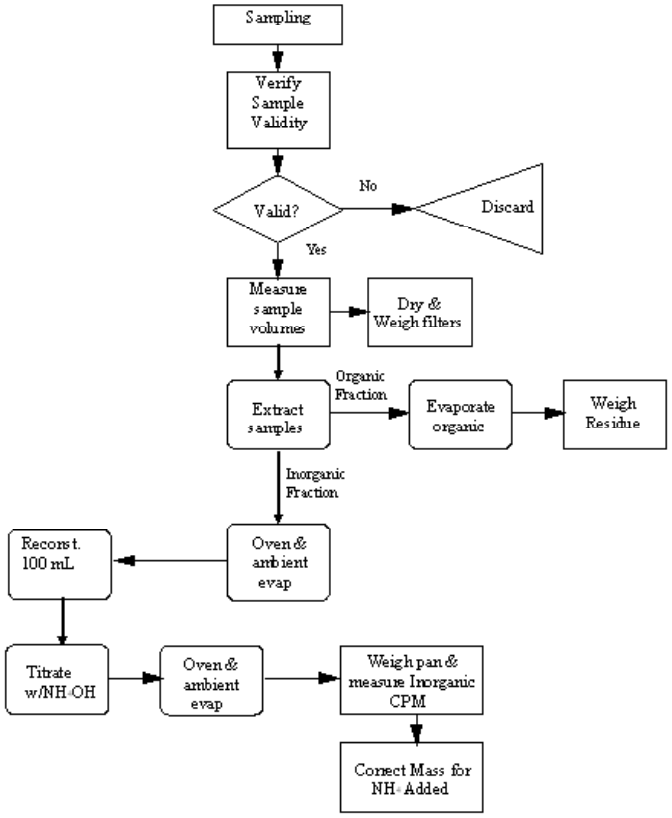



**Figure 11. Aqueous Impinger Sample Analysis Flow Chart**

**From:** <wrp6@daimlerchrysler.com> ***Index 25***
**To:** <Myers.Ron@epamail.epa.gov>, <Ray.Merrill@ERG.com>, <answers@ipass.net>
**Date:** Tue, Apr 3, 2007 10:08 AM
**Subject:** Clarification of Blanks - CTM20X

Ray:

As we discussed this morning, we repeated our study on oil mist collectors and the laboratory is currently on hold with the analysis until I provide them with a written method. Just prior to collecting the samples I obtained a copy of DRAFT CTM20X which has generated some questions because we rinsed the impingers with acetone, as the method called for.

Section 11, Analytical Procedures, specifically the blank determinations referenced in 11.2.10, 11.2.11, and 11.2.12 for acetone, water and methylene chloride respectively.

11.2.10 - Acetone blank is OK
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11.2.12 - CH2Cl2 blank states, "Analyze these samples as described in section 11.2.6.2 of this method".

11.2.6.1 refers to the extraction and tells us to add the water and methylene chloride (together with the acetone) to a separatory funnel.
11.2.6.2 refers to the Organic fraction weight determination.

Question 1 - Is it the intent of the draft method to mix the blanks? Ray, as we discussed, you thought not, but I want to make sure we're all on the same page before we go any further.

The next comment deals with the sample and blank correction. The addition of acetone to clean out the impingers before the methylene chloride rinse is an additional variable to take into consideration and the method should be clear that all blank reagents, water, acetone and methylene chloride must be normalized to mass. It appears this is addressed by the use of exactly 100 mL of each blank, but perhaps the method should state clearly the volume to eliminate any confusion or mishandling of the blanks with respect to blank subtraction.

Question 2 - deals with what is happening to the acetone in the separatory funnel. Are we interested in where the acetone goes, be it the water, or methylene chloride? If no, and all that really matters is the final mass, then why do we separate the inorganics from the organics for this type of application? Why not simply dry down and record?

I'd appreciate a quick response to question 1 so the laboratory can move forward with the analysis.

Thank you!

William R. Prokopy
DaimlerChrysler Corporation
Manager, Environmental Laboratory and Testing Services
T/L 722-8820

248-512-8820

**From:** Ray Merrill ***Index 26***
**To:** myers.ron@epa.gov
**Date:** Wed, Apr 4, 2007 5:13 PM
**Subject:** Fwd: Clarification of Blanks - CTM20X

Ron
In response to Bill's question # 1, I have attached a word perfect rewrite of sections 11.2.10, 11.2.11, and 11.2.12 that contain the procedure for determining the residual weight of the reagent solvents used to recover samples from the combined Method 201/202. Upon review and from our discussion, we've rewritten these three paragraphs to stand alone rather than refer to other procedures in the method.

We're recommending two fundamental changes: First, a known quantity of reagent blank (water, acetone, and methylene chloride) should be evaporated to dryness without regard to organic or inorganic residual contents. That means the water does not need to be extracted with methylene chloride to divide the blank between organic and inorganic material. Second, per your recommendation to follow Method 315, we've changed the procedure to require drying the sample in a desiccator for 24 hours followed by a single weighing to 0.1 mg rather than a requirement to weight to a constant weight.

Please review the attached text and if you agree with these changes, please feel free to forward them on to Bill at daimler chrysler
We will continue to track changes in a marked up electronic version of the full method.

We'll also continue to work with you on responses to Bill's other questions.

Ray
Eastern Research Group
919 468 7887

>>> <wrp6@daimlerchrysler.com> 4/3/2007 9:58 AM >>>

Ray:

As we discussed this morning, we repeated our study on oil mist collectors and the laboratory is currently on hold with the analysis until I provide them with a written method. Just prior to collecting the samples I obtained a copy of DRAFT CTM20X which has generated some questions because we rinsed the impingers with acetone, as the method called for.

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11.2.6.1 refers to the extraction and tells us to add the water and methylene chloride (together with the acetone) to a separatory funnel.
11.2.6.2 refers to the Organic fraction weight determination.

Question 1 - Is it the intent of the draft method to mix the blanks? Ray, as we discussed, you thought not, but I want to make sure we're all on the same page before we go any further.

The next comment deals with the sample and blank correction. The addition of acetone to clean out the impingers before the methylene chloride rinse is an additional variable to take into consideration and the method should be clear that all blank reagents, water, acetone and methylene chloride must be normalized to mass. It appears this is addressed by the use of exactly 100 mL of each blank, but perhaps the method should state clearly the volume to eliminate any confusion or mishandling of the blanks with respect to blank subtraction.

Question 2 - deals with what is happening to the acetone in the separatory funnel. Are we interested in where the acetone goes, be it the water, or methylene chloride? If no, and all that really matters is the final mass, then why do we separate the inorganics from the organics for this type of application? Why not simply dry down and record?

I'd appreciate a quick response to question 1 so the laboratory can move forward with the analysis.

Thank you!

William R. Prokopy
DaimlerChrysler Corporation
Manager, Environmental Laboratory and Testing Services
T/L 722-8820
248-512-8820

**CC:** Fanjoy, Joe; Merrill, Ray

11.2.10 Analysis of Acetone Blank (Container No. 10). Use 100 mL of acetone from the blank container for this analysis. If insufficient liquid is available or if the water has been lost due to container breakage either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer 100 mL of the acetone to a clean 250 mL beaker. Evaporate the acetone at room temperature and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50 mL preweighed tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg.

11.2.11 Analysis of Water (Container #11). Use 100 mL of the water from the blank container for this analysis. If insufficient liquid is available or if the water has been lost due to container breakage either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the water to a clean 250 mL beaker and evaporate to approximately 10 mL liquid in the oven at 105 °C. Quantitatively transfer the beaker contents to a clean preweighed 50 mL tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg

11.2.12 Analysis of Methylene Chloride Blank (Container Nos. 12). Use 100 mL of methylene chloride from the blank container for this analysis. Transfer 100 mL of the methylene chloride to a clean 250 ml beaker. Evaporate the methylene chloride at room temperature and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50 mL preweighed tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg.

***Index 27***

**From:** <Myers.Ron@epamail.epa.gov>
**To:** <wrp6@daimlerchrysler.com>
**Date:** Wed, Apr 4, 2007 6:05 PM
**Subject:** Re: Clarification of Blanks - CTM20X

Bill:

I have attached a PDF file with a rewrite of sections 11.2.10, 11.2.11, and 11.2.12 that contain the procedure for determining the residual weight of the reagent solvents used to recover samples from the combined Method 201/202. Upon review and from a discussion with Ray Merrill, and we've rewritten these three paragraphs to stand alone rather than refer to other procedures in the method.

You will notice that we're making two fundamental changes: First, a known quantity of reagent blank (water, acetone, and methylene chloride) should be evaporated to dryness without regard to organic or inorganic residual contents. That means the water does not need to be extracted with methylene chloride to divide the blank between organic and inorganic material. Second, as with EPA Method 315 (developed to determine organic extractable material for aluminum smelters), we've changed the procedure to require drying the sample in a desiccator for 24 hours followed by a single weighing to 0.1 mg rather than a requirement to weight to a constant weight.

(See attached file: M 20X Blank solvent analysis.pdf)

This should answer your first question.

For your second question, I will need to review the draft 20X methodology. In Method 315, the acetone/methylene chloride rinse of the impingers does not get recombined with the major portion of the water from the impingers. It is dried and weighed separately. I will need to consult Gary and Ray to see what revisions of the existing write up are needed. Since the final drying is at room temperature and we are primarily interested in total mass and not separate inorganic and organic mass we may propose an alternative procedure at least for the acetone/methylene chloride rinses of the impingers. I will talk to Ray and Gary tomorrow and get back to you.

_____

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

wrp6@daimlerchry
sler.com

To

04/03/2007 09:58 Ron Myers/RTP/USEPA/US@EPA,

AM Ray.Merrill@ERG.com,
answers@ipass.net
cc

Subject
Clarification of Blanks - CTM20X

Ray:

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248-512-8820

**CC:** <answers@ipass.net>, <Ray.Merrill@ERG.com>, <Logan.Thomas@epamail.epa.gov>, <Gary_McAlister/RTP/USEPA/US@mintra02.rtp.epa.gov>, <Sorrell.Candace@epamail.epa.gov>

11.2.10 Analysis of Acetone Blank (Container No. 10). Use 100 mL of acetone from the blank container for this analysis. If insufficient liquid is available or if the water has been lost due to container breakage either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer 100 mL of the acetone to a clean 250 mL beaker. Evaporate the acetone at room temperature and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50 mL preweighed tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg.

11.2.11 Analysis of Water (Container #11). Use 100 mL of the water from the blank container for this analysis. If insufficient liquid is available or if the water has been lost due to container breakage either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the water to a clean 250 mL beaker and evaporate to approximately 10 mL liquid in the oven at 105 °C. Quantitatively transfer the beaker contents to a clean preweighed 50 mL tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg

11.2.12 Analysis of Methylene Chloride Blank (Container Nos. 12). Use 100 mL of methylene chloride from the blank container for this analysis. Transfer 100 mL of the methylene chloride to a clean 250 ml beaker. Evaporate the methylene chloride at room temperature and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50 mL preweighed tin and evaporate to dryness at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh and report the results to the nearest 0.1 mg.

**From:** <Myers.Ron@epamail.epa.gov> **Index 28**
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Fri, Apr 6, 2007 6:55 PM
**Subject:** Re: SES

**CC:** "Jim Meador" <jmeador@testair.com>, "Ray Merrill" <Ray.Merrill@erg.com>, <Logan.Thomas@epamail.epa.gov>, <Sorrell.Candace@epamail.epa.gov>, <Schell.Bob@epamail.epa.gov>, <Oldham.Conniesue@epamail.epa.gov>, <Mcalister.Gary@epamail.epa.gov>

***Index 29***

**From:** <Myers.Ron@epamail.epa.gov>
**To:** "Moll, David" <DMoll@ensr.aecom.com>
**Date:** Wed, Apr 11, 2007 6:46 PM
**Subject:** Re: Questions on dry impinger method 202

David:
I am sorry that I did not return your call. I have been in meetings almost all day. I have provided answers to your questions in blue text below the question. If I heard your voice mail correctly, you are doing this work for Bob Hall in ORD. I don't know the details of your test program, but I am including a copy of the latest draft that I am reviewing in this message as well. Also, to complete the loop, I am copying Bob so that he knows that I have provided you the draft method. You should know that we have encountered several issues with blanks and obtaining low solids reagents.

(See attached file: DRAFT Method 20X 3-19-07.pdf)

Also, I have attached a PDF file with a rewrite of sections 11.2.10, 11.2.11, and 11.2.12 that contain the procedure for determining the residual weight of the reagent solvents used to recover samples from the combined Method 201/202. Upon review and from a discussion with Ray Merrill, and we've rewritten these three paragraphs to stand alone rather than refer to other procedures in the method.

You will notice that we're making two fundamental changes: First, a known quantity of reagent blank (water, acetone, and methylene chloride) should be evaporated to dryness without regard to organic or inorganic residual contents. That means the water does not need to be extracted with methylene chloride to divide the blank between organic and inorganic material. Second, as with EPA Method 315 (developed to determine organic extractable material for aluminum smelters), we've changed the procedure to require drying the sample in a desiccator for 24 hours followed by a single weighing to 0.1 mg rather than a requirement to weight to a constant weight.

(See attached file: M 20X Blank solvent analysis.pdf)

If you could, would you suggest participation in our stakeholder effort to expand the number of sources that we are engaging in this process. I would think that this might be as little as running dual trains on the source that you are testing in order to obtain precision data for this method. Also, our experience with Method 202 has been that there is always one run out of a dozen that we can not explain because it is different from the remainder. Running dual trains offers the advantage of identifying whether that is a measurement error or just a variation in the process.

Lastly, I have copied this to others on the EPA team and Ray Merrill (my contractor). If you find anything in the method that could be stated better or that would improve the method let us know.

_____
Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards

Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

"Moll, David" <DMoll@ensr.aecom.com>
04/11/2007 03:01 PM

To: Ron Myers/RTP/USEPA/US@EPA
cc:
Subject: Questions on dry impinger method 202

Ron, I tried to reach you by phone but have not heard back. I am trying to finalize a technical approach for an upcoming program where we intend to use the dry impinger method 202 you have been working on. If you could help me answer the following questions it would be much appreciated.

Thanks Dave Moll
ENSR|AECOM
2 Technology Park Drive
Westford, MA 01886
978-589-3000, ext. 3508

1)What is the total number of impingers in the sampling train? I have seen different versions which use a different number of impingers.

There are a total of four impingers in the sampling train. The first two impingers are not maintained in the ice bath but are maintained as close to 85F as possible without exceeding that temperature. The trains that we have assembled and the ones used by one other tester have been in two sampling boxes but the equipment vendors have said that a large box could be used with a divider to separate the first two and last two impingers.

2) Are two separate water/ice baths required and what should the

condenser coil and knockout impinger temperature range be operated at? and what temperature range should the rest of the impingers and cold filter should be? Is the cold filter tarred and reweighed after sampling? I read 85F or less. Does this mean I can make it as low as I want, below 68F, which is typical for most sampling trains?

The first two impingers should not be in an ice bath. The rationale is that the solubility of SO2 in water is greater at the lower temperature and we want to inhibit as much as possible the amount of SO2 absorbed in the water. As a result you should run the first two impingers at as high of a temperature that you feel is reasonable to not exceed 85F at the exit of the filter following the first two impingers.

3)Please confirm that the purge includes the first impinger after replacing the stem to reach the knockout condensate and the condensate is part of the sample which is why it needs to be purged. One diagram we saw showed the purge location after the 1st impinger.

We purge both of the first two impingers. Yes all the condensate collected in the condenser and the first two impingers are part of the sample.

3) Is HPLC water used for the dry impinger Method 202 water rinses?

Absolutely, as I mentioned several people in this effort have encountered problems with solids in their reagents (water, acetone and methylene chloride). It would be wise to verify that the solids contents of any reagents that you use are absolutely insignificant. You could use manufactured laboratory water (doubly distilled and filtered) but you need to verify the quality of the water you produce.

**CC:** <Hall.Bob@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Sorrell.Candace@epamail.epa.gov>, <Ray.Merrill@erg.com>

***Index 30***

**From:** "Moll, David" <DMoll@ensr.aecom.com>
**To:** <Myers.Ron@epamail.epa.gov>
**Date:** Thu, Apr 12, 2007 3:33 PM
**Subject:** RE: Questions on dry impinger method 202

Ron, that you so much for the information and draft method. I recommended strongly to our client to participate in the program. I really appreciate the information. Our client has asked for us to prepare a list of experts which could review the abbreviated technical approach. I will certainly include you and your committee members listed on the QAPP.

Thanks again,

Dave Moll
ENSR|AECOM
2 Technology Park Drive
Westford, MA 01886
978-589-3000, Ext. 3508

-----Original Message-----
From: Myers.Ron@epamail.epa.gov [mailto:Myers.Ron@epamail.epa.gov]
Sent: Wednesday, April 11, 2007 6:39 PM
To: Moll, David
Cc: Hall.Bob@epamail.epa.gov; Logan.Thomas@epamail.epa.gov; Sorrell.Candace@epamail.epa.gov; Ray.Merrill@erg.com
Subject: Re: Questions on dry impinger method 202

David:
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Ron Myers
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Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

"Moll, David" <DMoll@ensr.aecom.com>
04/11/2007 03:01 PM

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**CC:** <Hall.Bob@epamail.epa.gov>, <Logan.Thomas@epamail.epa.gov>, <Sorrell.Candace@epamail.epa.gov>, <Ray.Merrill@erg.com>

**From:** "Marson,George (Jorge) [ETC]" <George.Marson@ec.gc.ca> ***Index 31***
**To:** "Ray Merrill" <Ray.Merrill@erg.com>
**Date:** Tue, Apr 17, 2007 4:35 PM
**Subject:** CPM results

Hi Ray

Some confirmatory results on the modified M 202

105oC OVEN DRYING WATER SOLUBLE CPM

| CPM | Spike recovery % | Dry heating loss %/hr | Desiccator loss %/day |
|---|---|---|---|
| glycerol | 101% | -22% | -1% |
| triethylene glycol | 100% | -45% | -3% |
| ammonia nitrate | 99% | -6% | -1% |
| ammonia chloride | 97% | -4% | -3% |

Had one instance of false end point (on ammonia nitrate) probably due to occluded solution.

My pipe dream of drying jointly MeCl2 rinses and condensate is an utter failure, even at 40oC.

Regards

George Marson, P.Eng.
QA & EMS Supervisor
phone (613) 991-9458
fax (613) 998-4032